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Wetting properties of polysiloxane networks modified in situ with fluoroalkyl-substituted linear and POSS cage structures

Raymond Campos, Sean M. Ramirez, and Joesph M. Mabry

August 17, 2015

ACS National Conference

Paradigms for low energy surfaces

Crystalline surfaces

- Immobilized chemical moieties with low polarizability (e.g. fluorine)

  $CF > CF_2 > CF_3 > SF_5$

- High crystallinity to prevent surface reorganization when in contact with liquids, biofouling sources, etc.

Extreme liquid repellency when combined with surface roughness and re-entrant geometry

"liquid-like" surfaces

- low energy barriers between metastable states

- Metal oxide surfaces and liquid-infused materials (e.g. SLIPS)

Fluorine content not required to repel low surface tension liquids?

Low CA hysteresis despite lower contact angle values

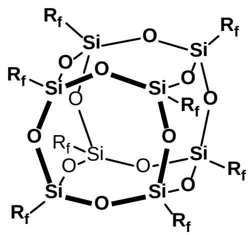
Surface modification of PDMS/siloxane networks

- Primarily oxide formation via O_2 plasma, UV/ozone, etc. and subsequent functionalization

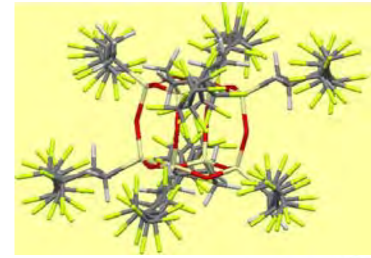
- Functional PDMS (e.g. residual vinyl groups in network)

- Functional silsesquioxane networks

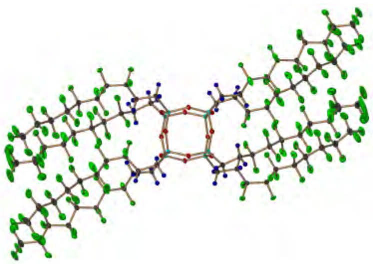
Properties of Fluorodecyl$_8$T$_8$ POSS

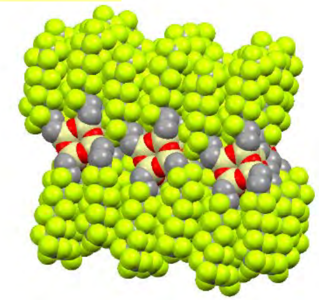


$R_f = {}^-(CH_2)_2(CF_2)_8F$

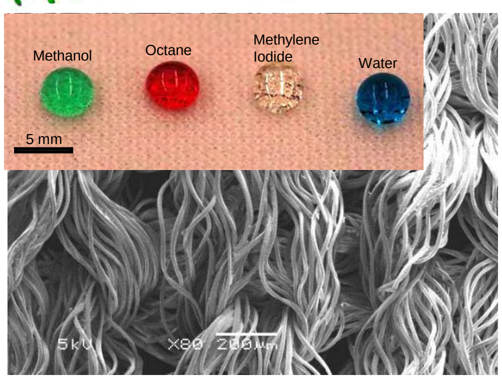


- Extremely low surface energy
- Surface migration in polymers
- Surface responsive behavior



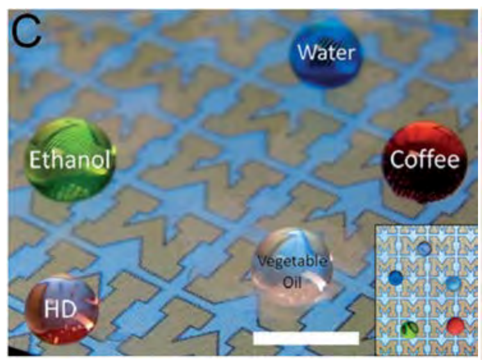


Enabling….



Superomniphobic fabrics via dip-coating

Choi *et al., Ang. Chem.*, 2009

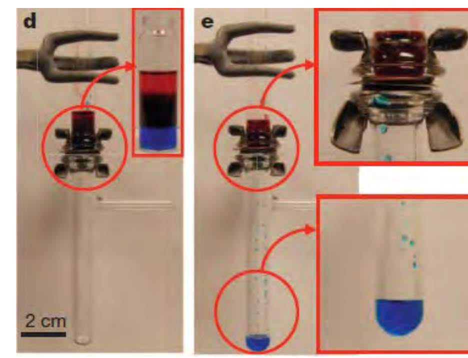


Transparent Omniphobicity

Golovin *et al., Ang. Chem.*, 2013

Extreme Omniphobicity

Pan *et al., JACS.*, 2012



Oil/water emulsion gravity seperation

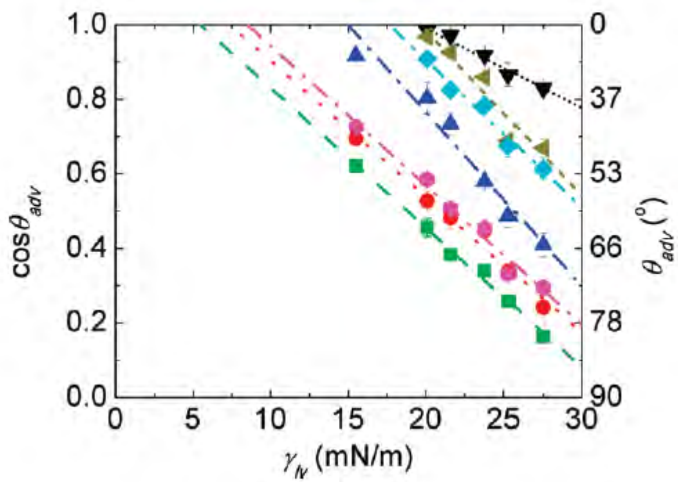
Kota *et al., JACS.*, 2012

Surface Energy of Fluorodecyl$_8$T$_8$ POSS

fluorodecyl$_8$T$_8$ POSS

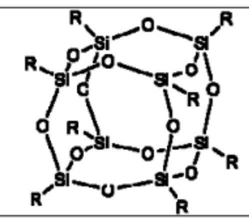
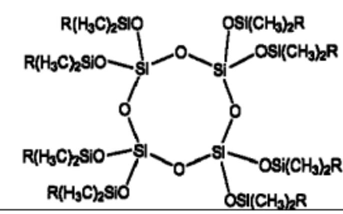
5.5 mN/m (Zisman analysis)*

8.8 – 10.2 mN/m (Girafalco-Good analysis)*



Zisman analysis

(only alkane probing liquids used)

	Fluorodecyl T_8, R = $-(CH_2)_2-(CF_2)_7-CF_3$ Fluorooctyl T_8, R = $-(CH_2)_2-(CF_2)_5-CF_3$ Fluorohexyl T_8, R = $-(CH_2)_2-(CF_2)_3-CF_3$ Fluoropropyl T_8, R = $-(CH_2)_2-CF_3$ Hexafluoro-*i*-butyl T_8, R = $-CH_2-CH(CF_3)_2$
	Fluorodecyl Q_4, R = $-(CH_2)_2-(CF_2)_7-CF_3$
$F_3C(F_2C)_7(H_2C)_2(H_3C)_2Si-O-Si(CH_3)_2(CH_2)_2(CF_2)_7CF_3$	Fluorodecyl M2, R = $-(CH_2)_2-(CF_2)_7-CF_3$

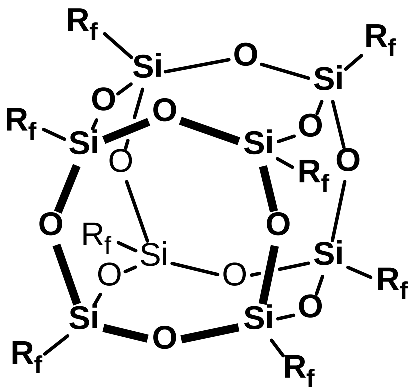
*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Fluoroalkylated Silicon-Containing Surfaces-Estimation of Solid-Surface Energy. *ACS Applied Materials and Interfaces* 2010, *2* (12), 3544-3554.

Surface Energy of Fluorodecyl$_8$T$_8$ POSS

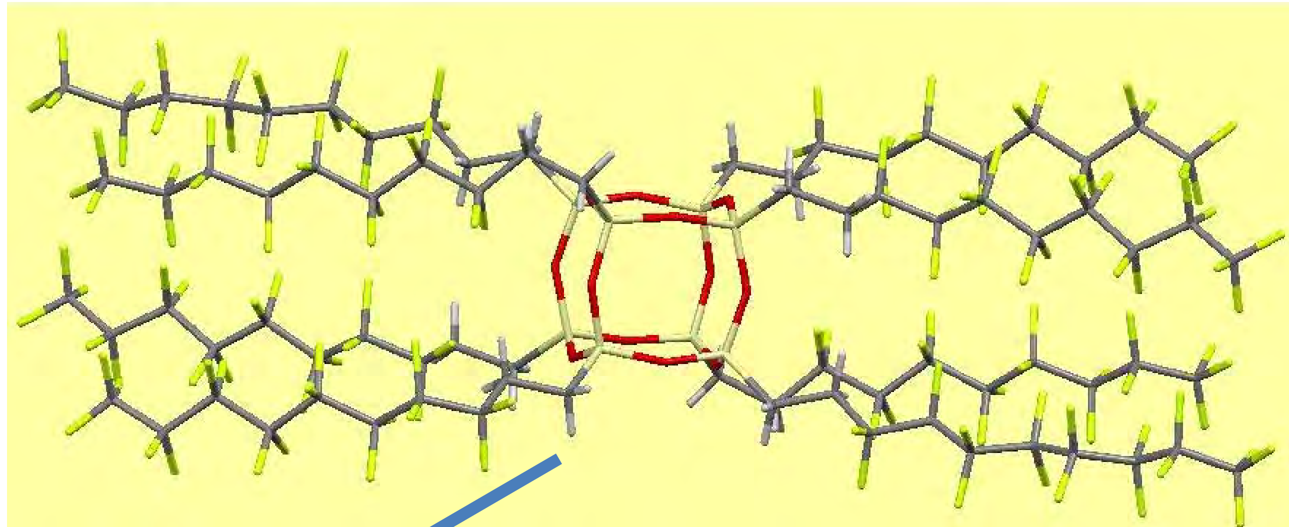
fluorodecyl$_8$T$_8$ POSS	5.5 mN/m (Zisman analysis)* 8.8 - 10.2 mN/m (Girafalco-Good analysis)*
Polytetrafluoroethylene CF_3-$(CF_2)_n$-CF_3	18 - 20 mN/m (Zisman analysis)
CF_3 monolayer	6.7 mN/m (Zisman analysis)

Why?

*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Fluoroalkylated Silicon-Containing Surfaces-Estimation of Solid-Surface Energy. *ACS Applied Materials and Interfaces* 2010, *2* (12), 3544-3554.



$R_f = {}^{-}(CH_2)_2(CF_2)_8F$



Fluorodecyl$_8$T$_8$ POSS

Rotate ~ 90°

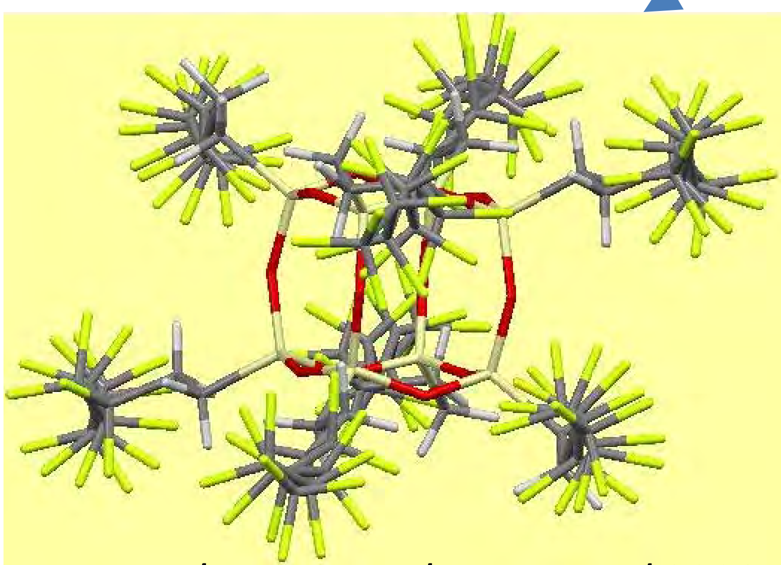
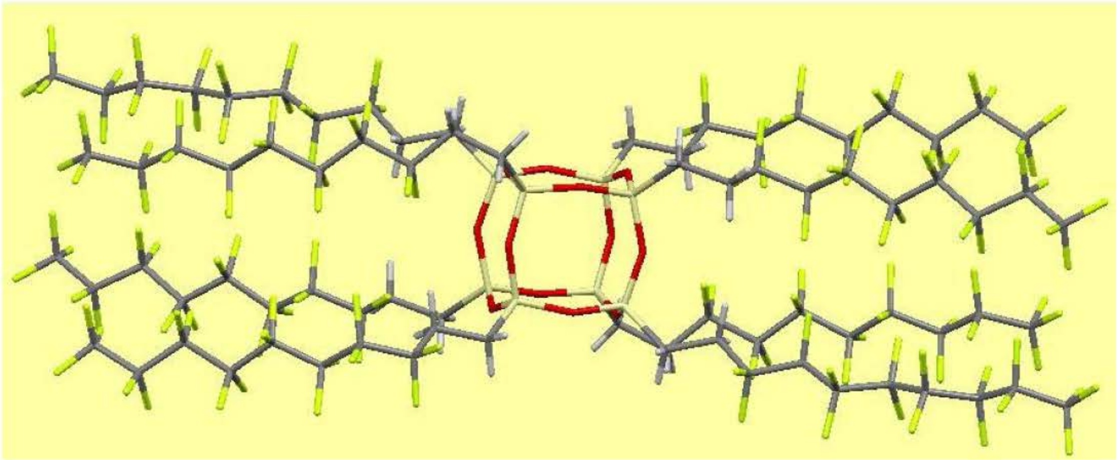
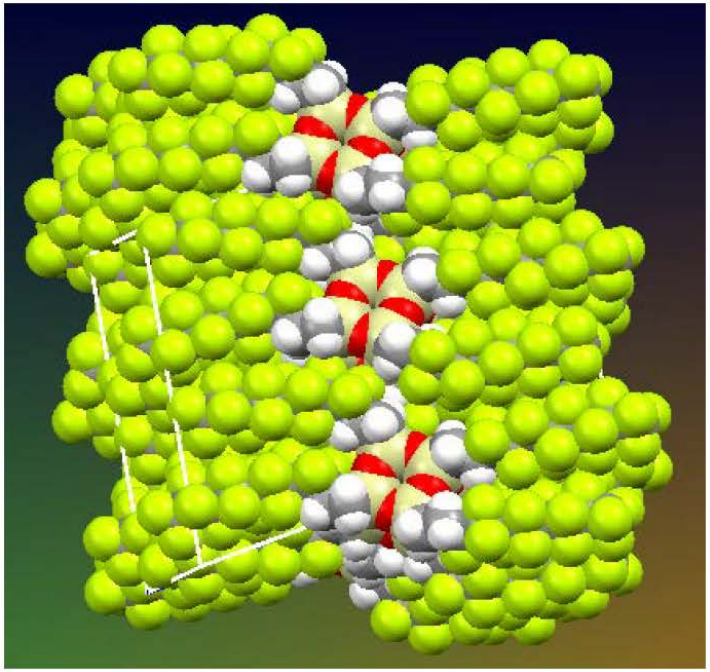
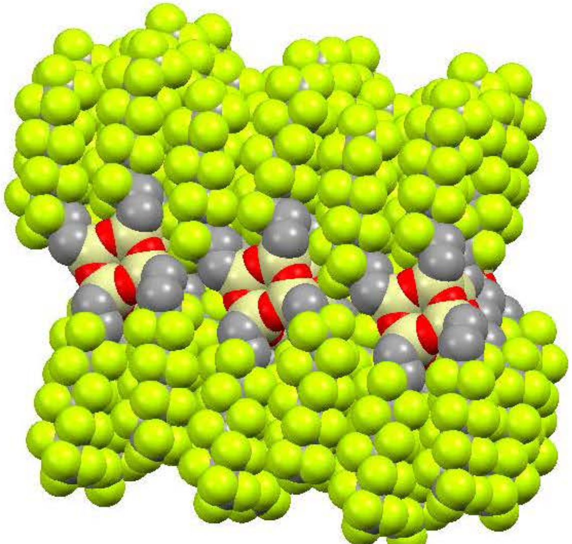


Image displaying the helical conformation of fluorodecyl substituents in the solid state packing of fluorodecyl$_8$T$_8$ POSS

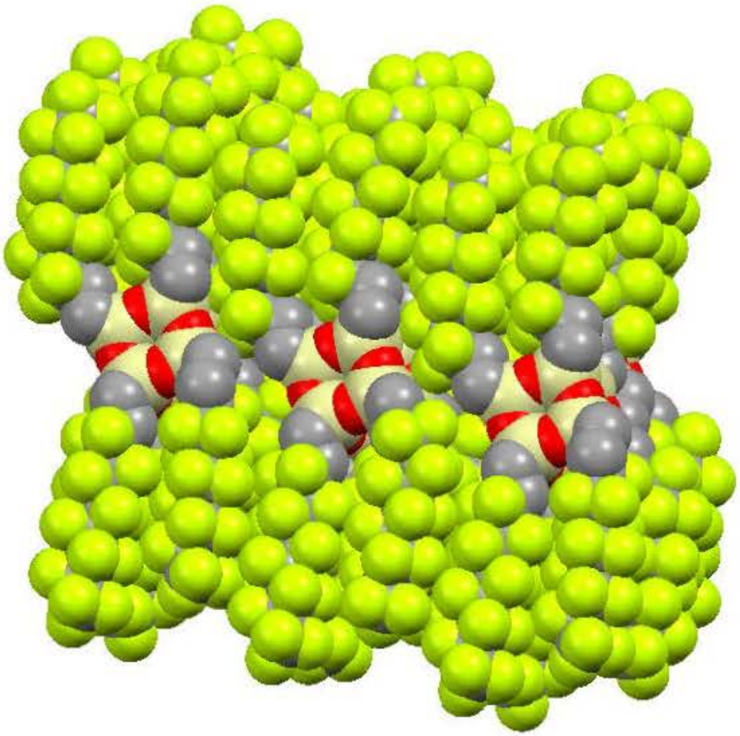
Mabry, J. M. *et al.*, *Angew. Chem. Int. Ed* **2008,** *47*, 4137-4140

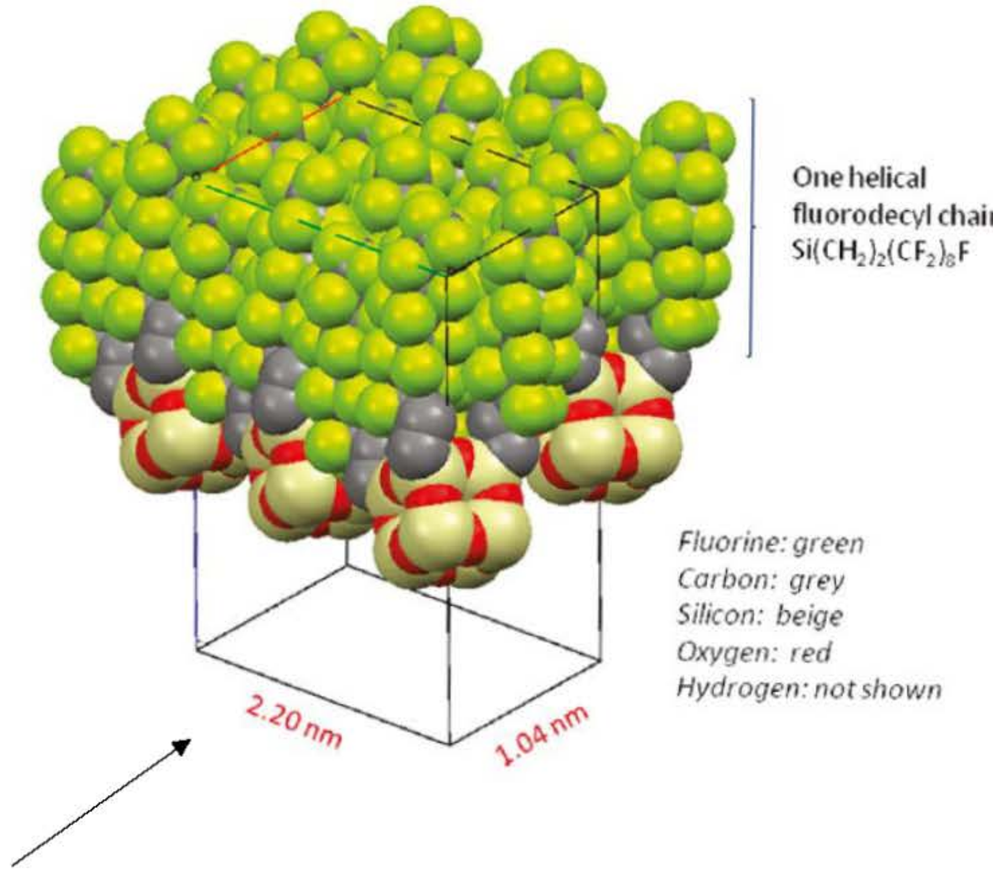




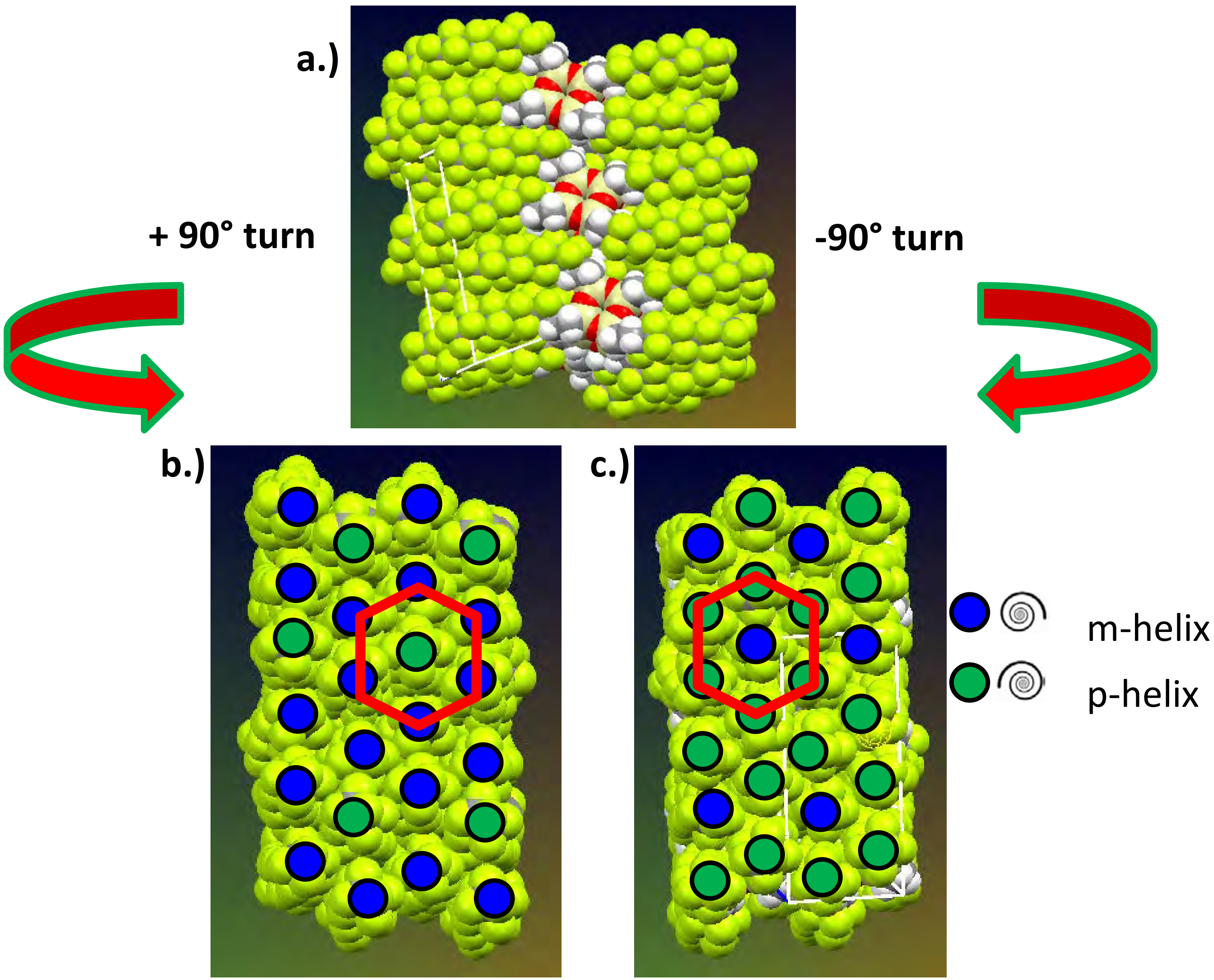


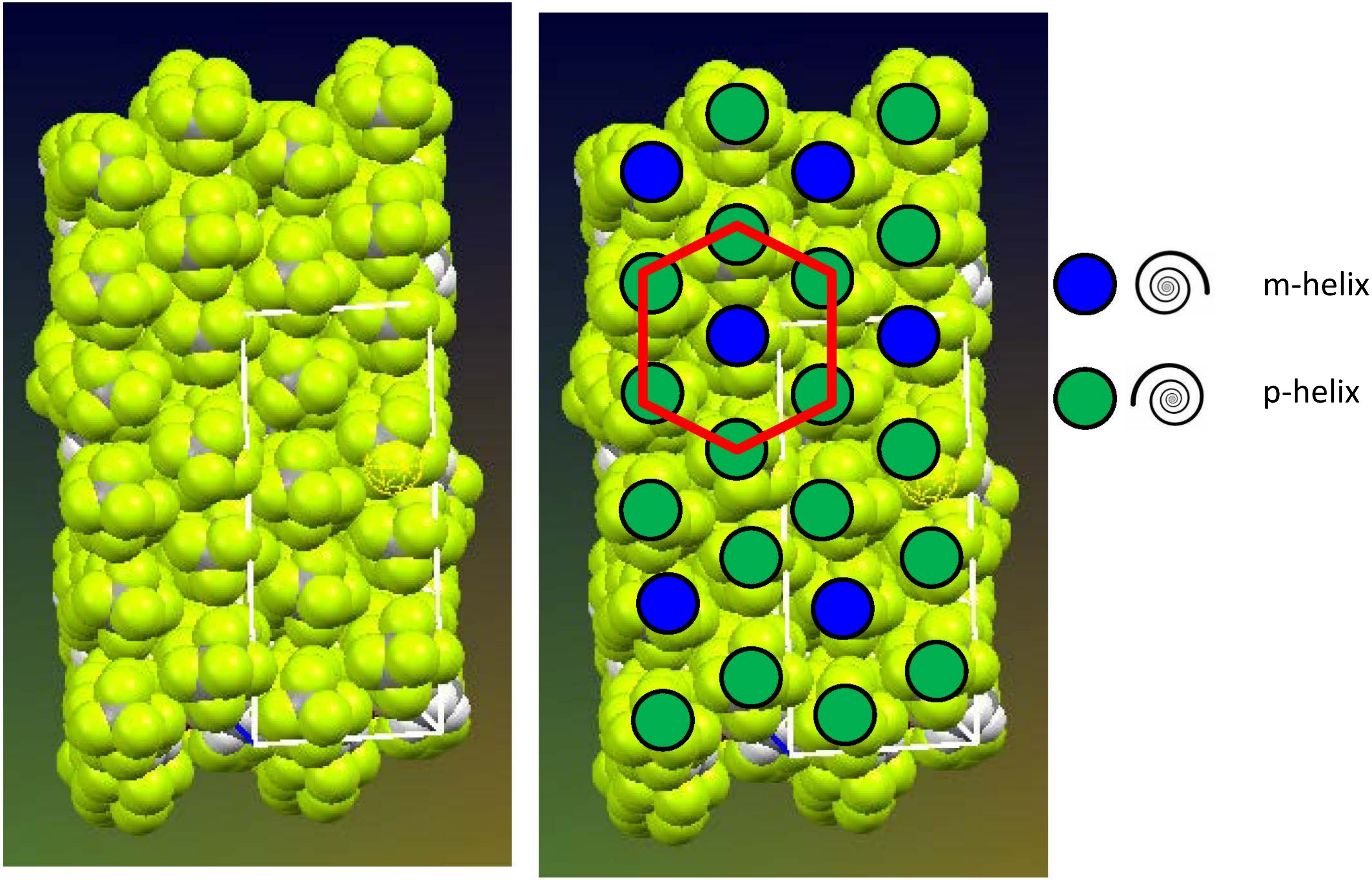
3 x 2 array of fluorodecyl8T8 POSS cages displaying a lamella-type packing



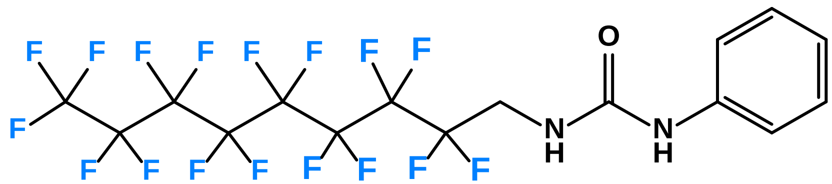


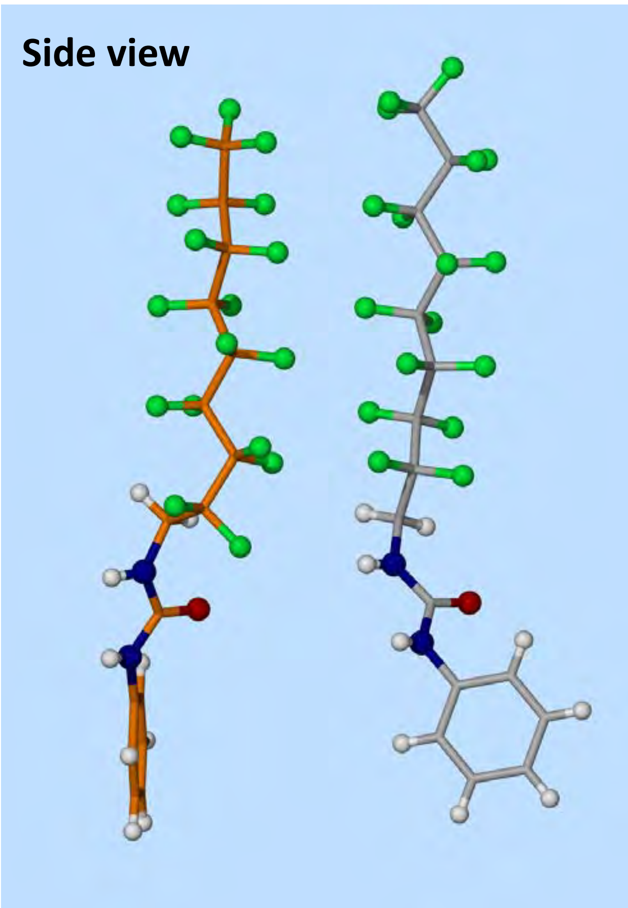
Campos, R., Haddad T. S., *et al.*, *Langmuir* **2011,** *27* (16), 10206-10215.

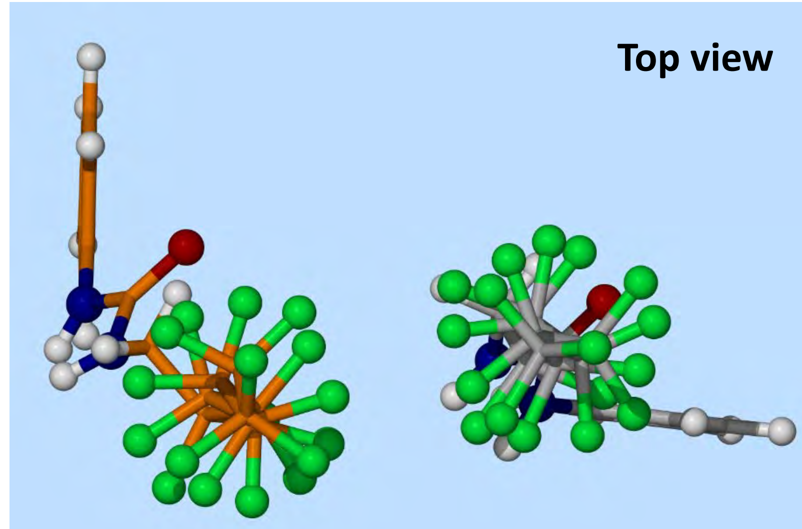

a.)
+ 90° turn
-90° turn
b.)
c.)
m-helix
p-helix

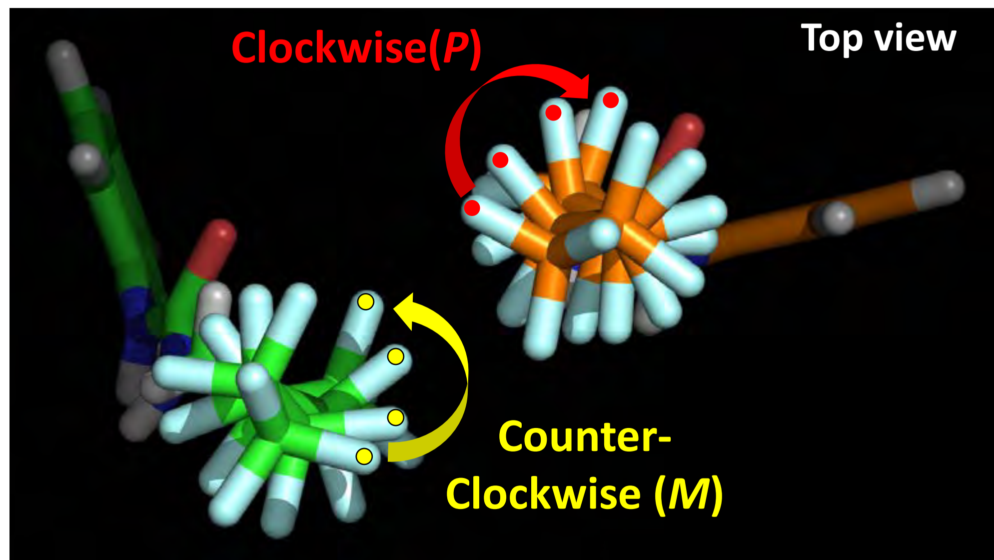

m-helix
p-helix

Helical crystal packing of fluoroalkyl-substituted urea

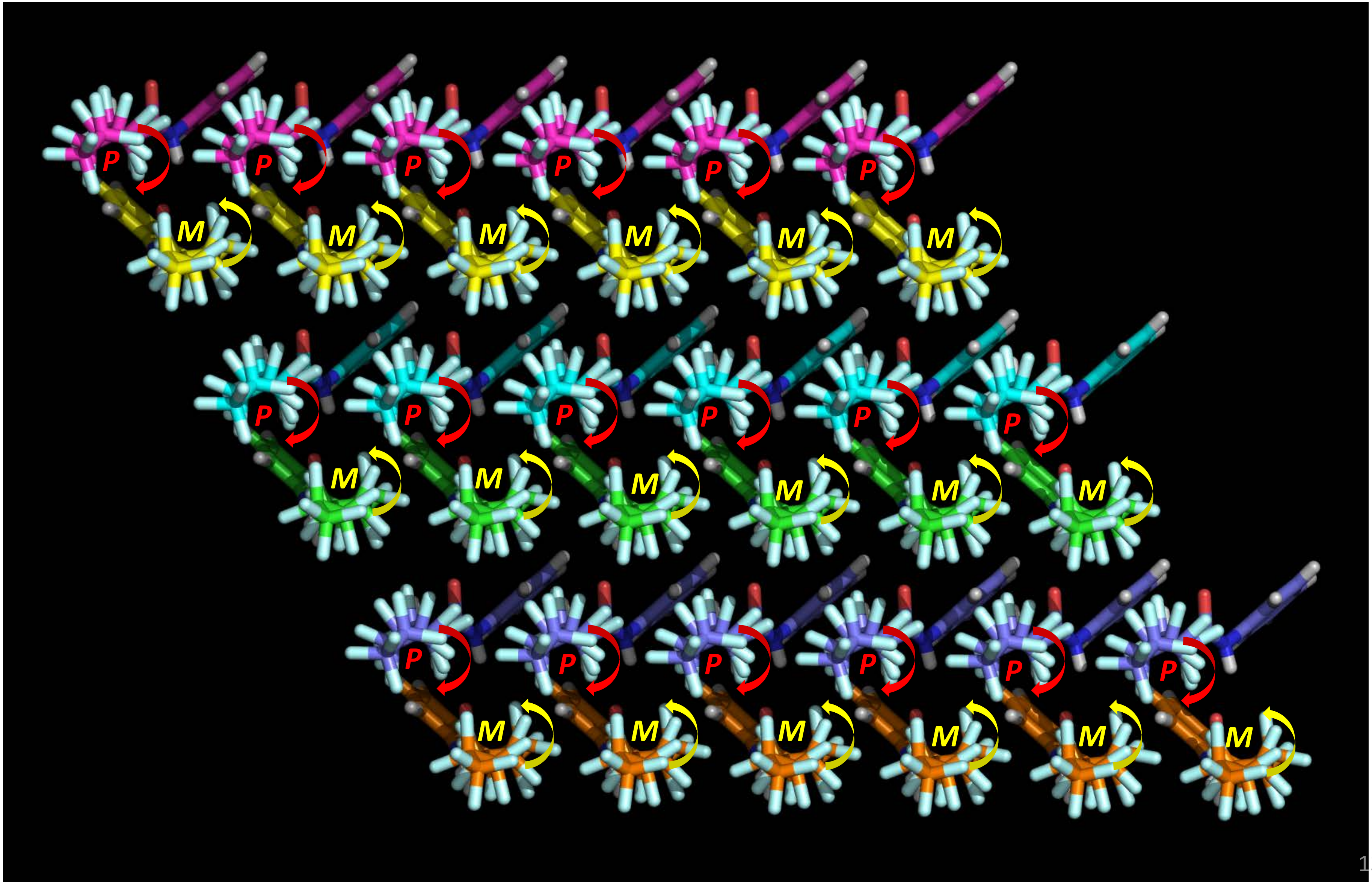






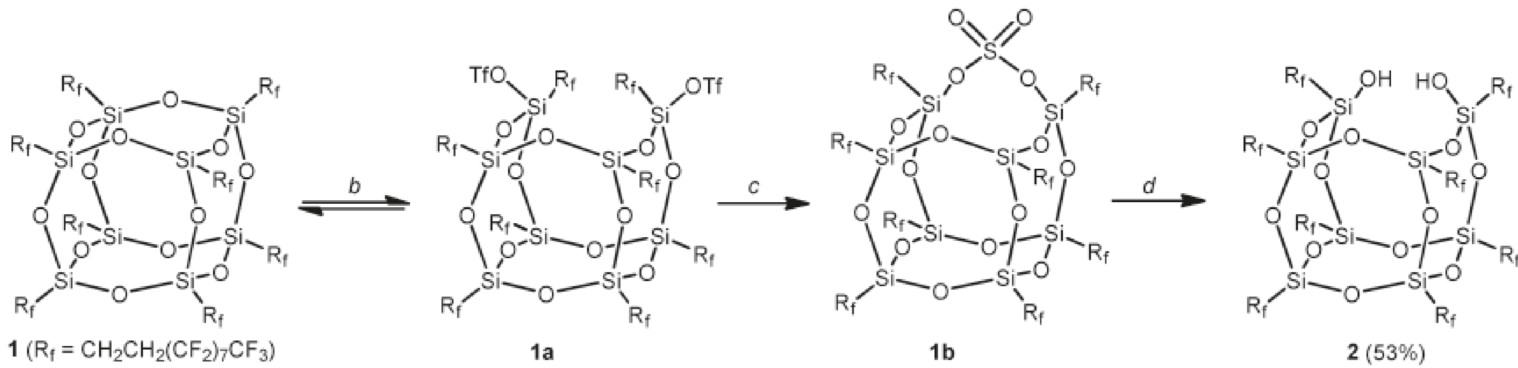


Helical crystal packing of fluoroalkyl-substituted urea



Functional Fluorodecyl POSS Compounds Enabled by Incompletely Condensed Intermediate

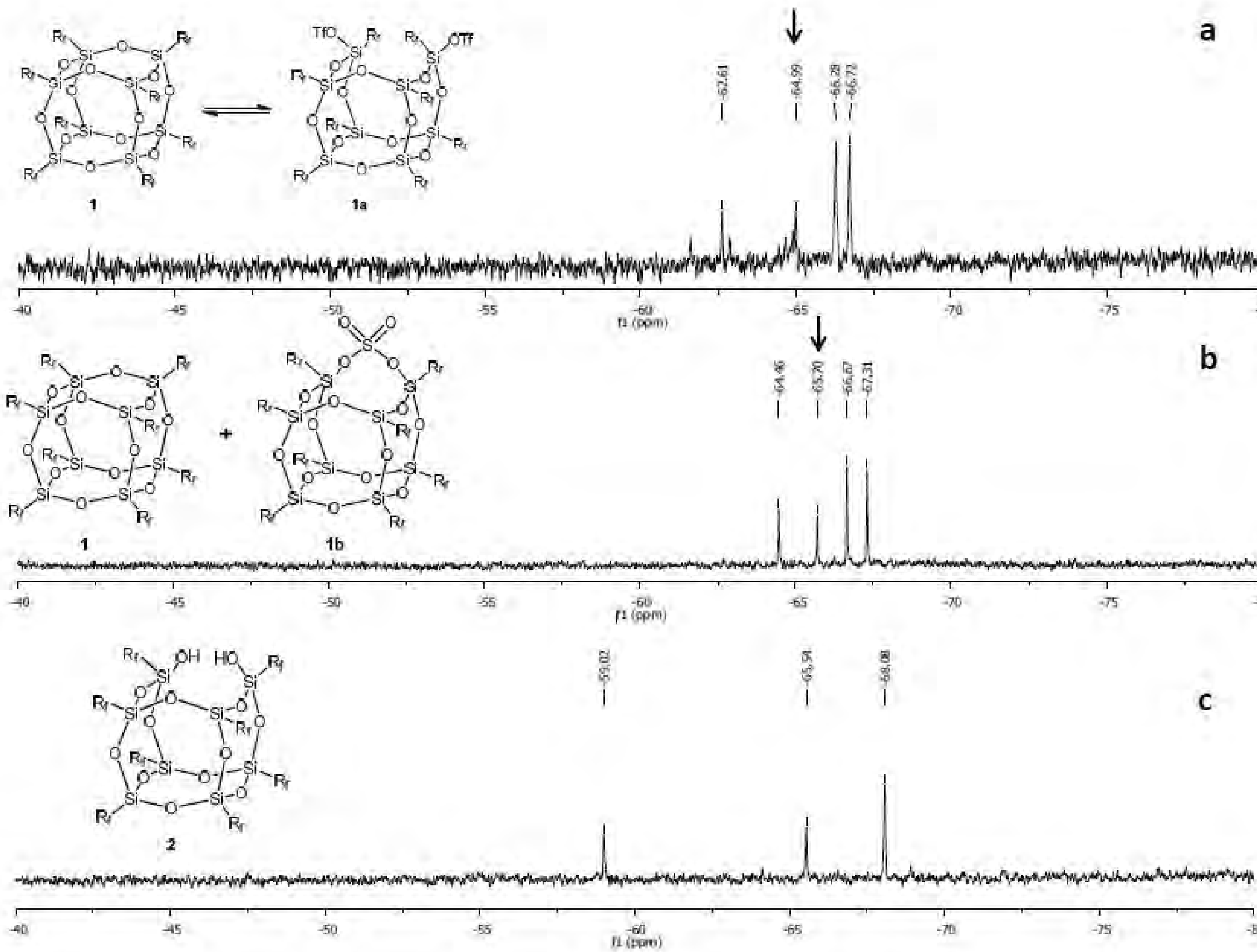
Scheme 1. Synthesis of Incompletely Condensed Fluoroalkyl Silsesquioxane[a]



[a] Conditions: All reactions were performed in C_6F_6 at 25 °C. [b]CF_3SO_3H, 75 min; [c]$NBut_4HSO_4$, 30 min; [d]$(CF_3)_2CH_2OH/H_2O$ (10:1), 12 h.

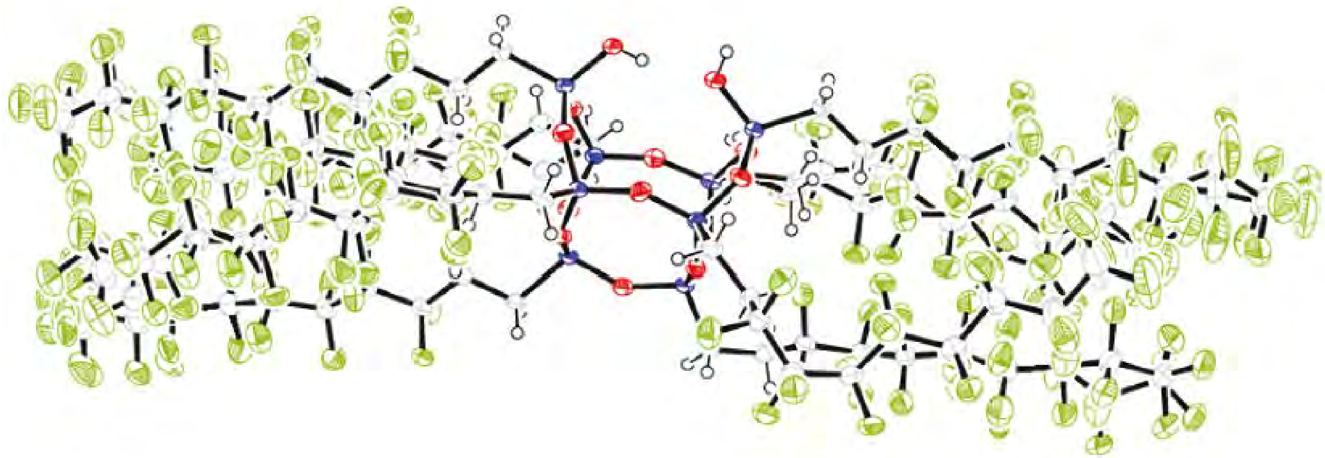
Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS,* **2011**, *133*, 20084.

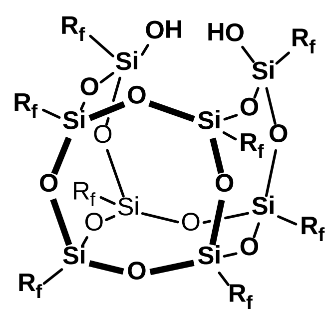
^{29}Si NMR Spectra of fluorodecyl POSS disilanol Intermediates and Product



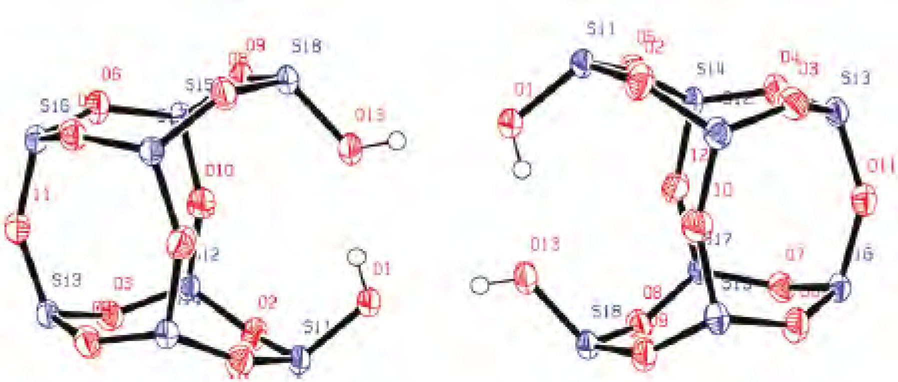
Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS,* 2011, *133*, 20084.

ORTEP representations of Fluorodecyl POSS Disilanol crystal structure



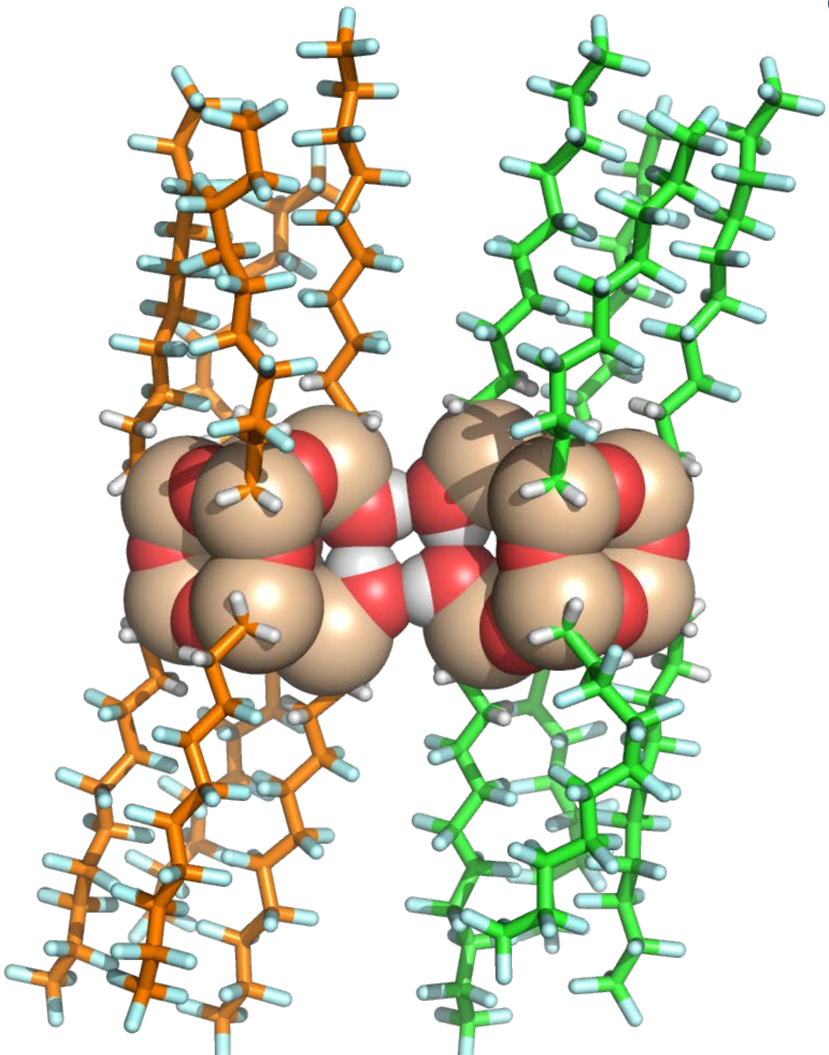


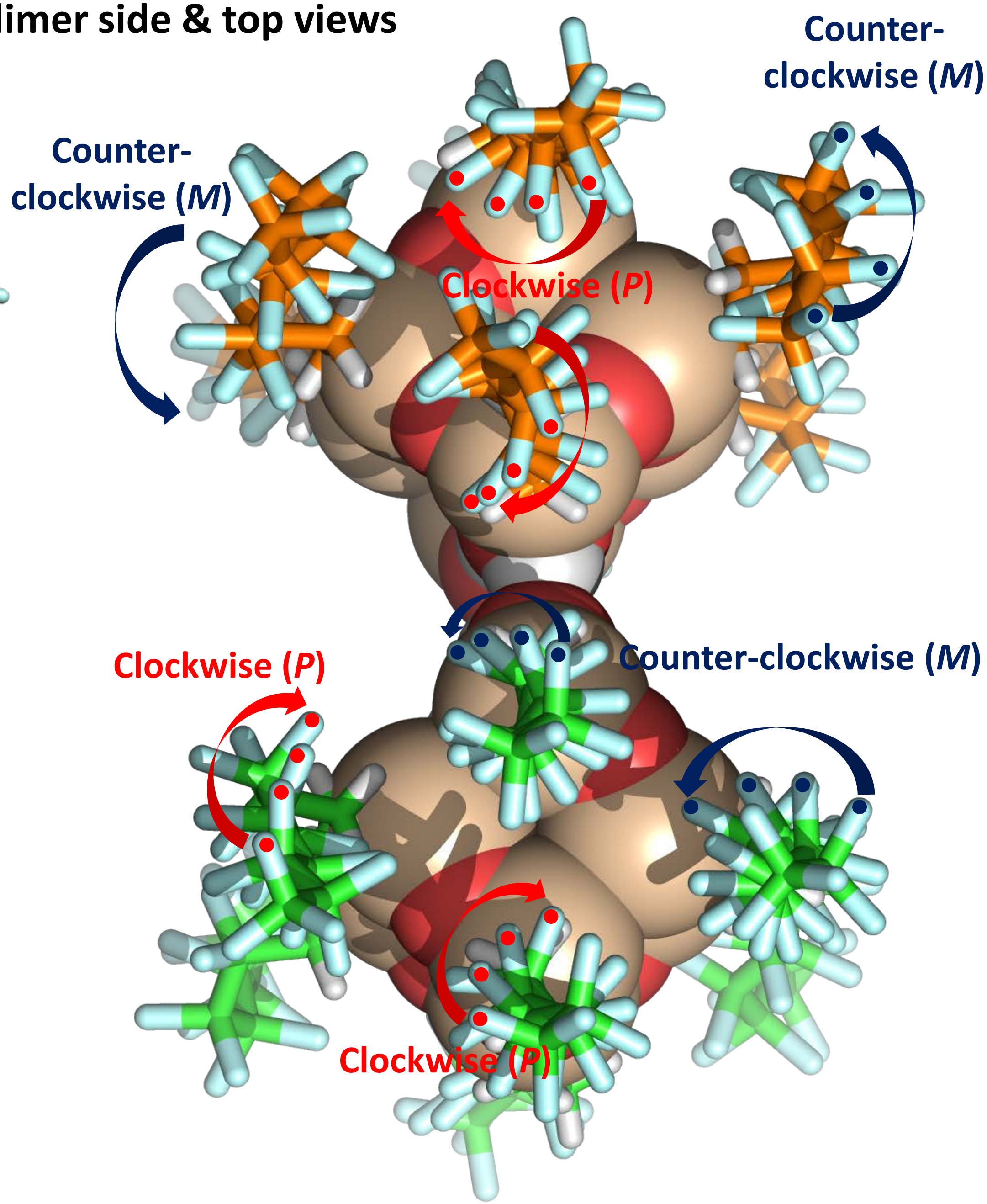
$R_f = {}^{-}(CH_2)_2(CF_2)_8F$



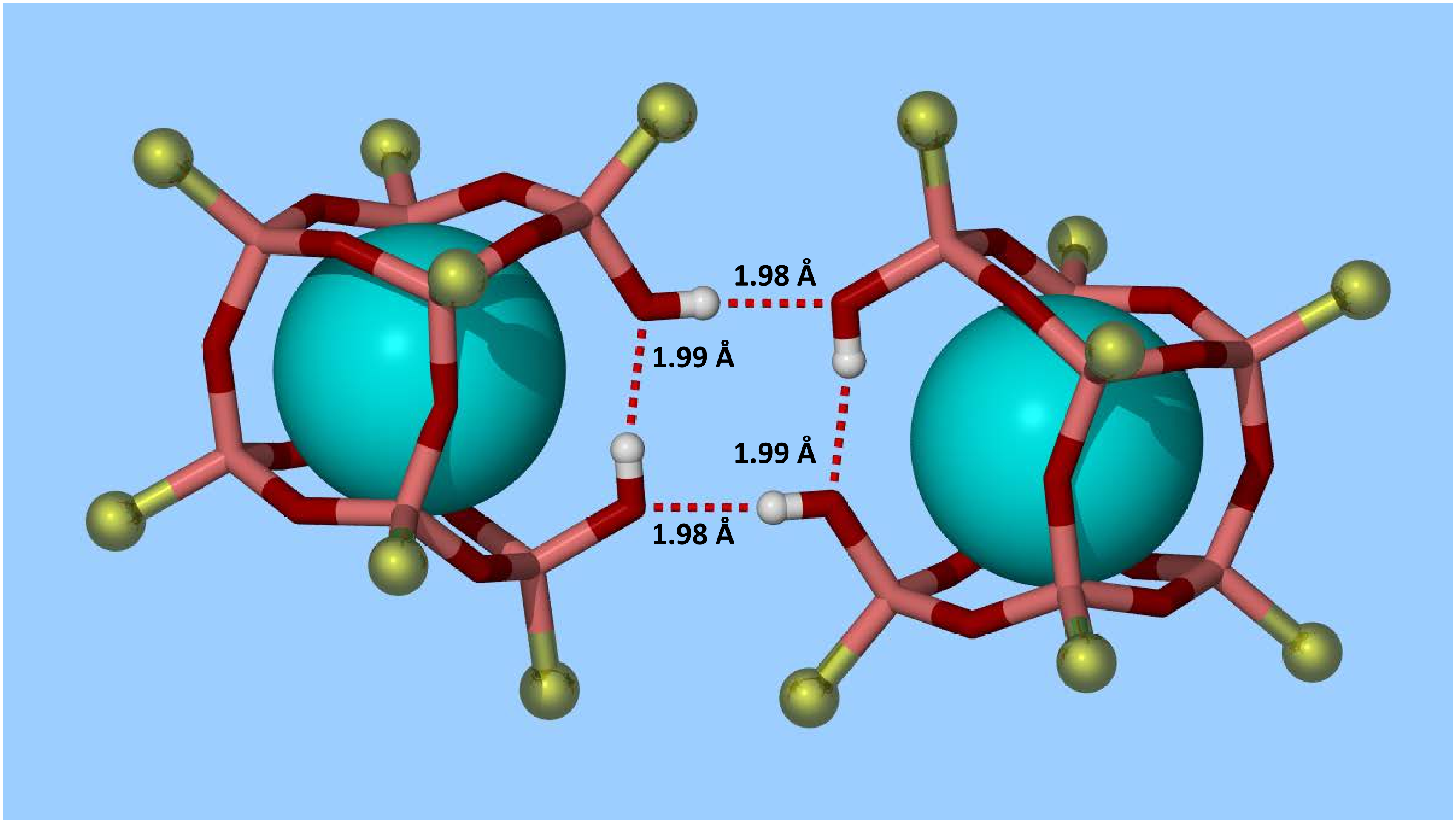
Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS,* 2011, *133*, 20084.

F-POSS cage dimer side & top views

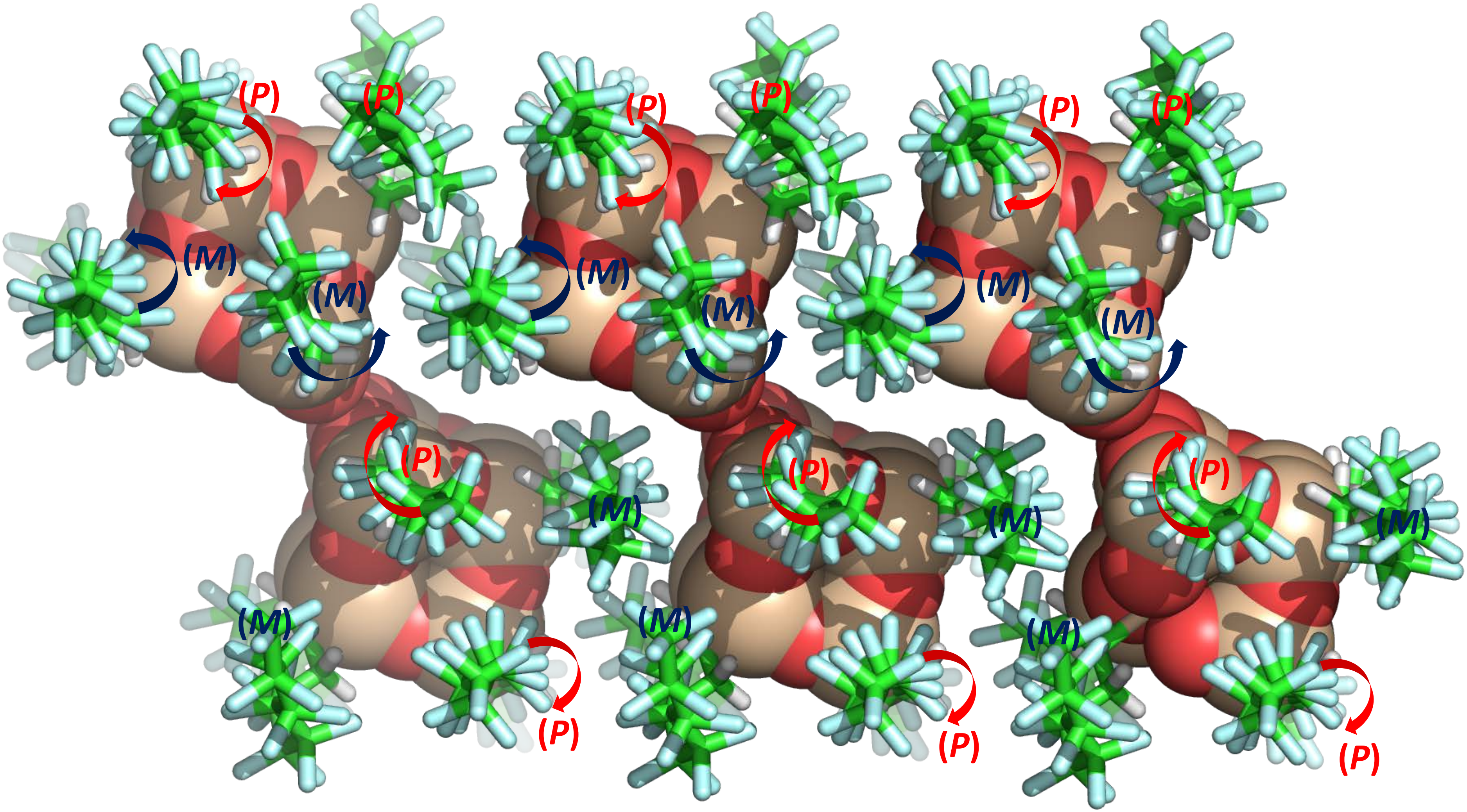




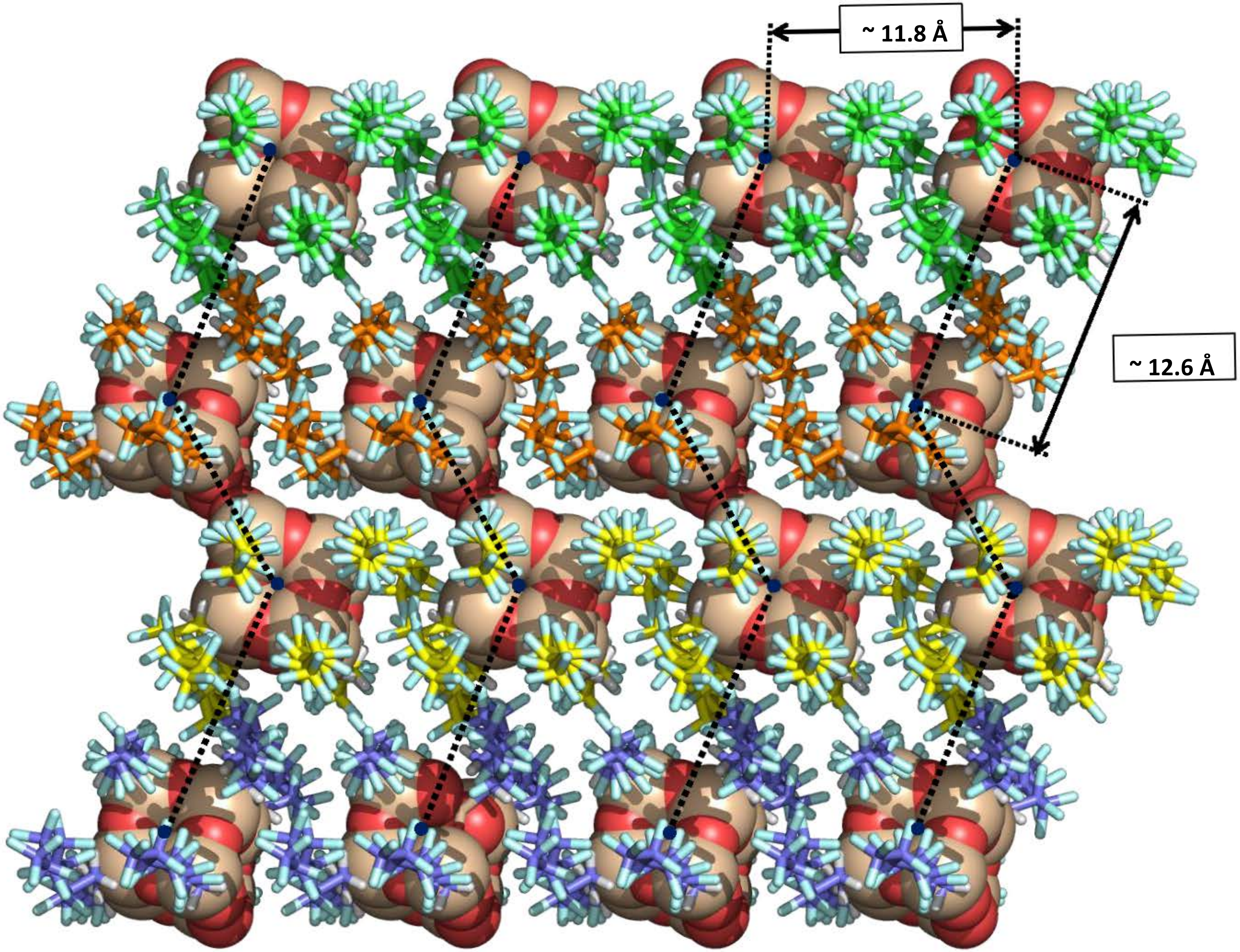
F-POSS cage dimer (fluoroalkyl side chains shown as golden spheres): 2 intermolecular OH…O - bonds that hold dimer structure together



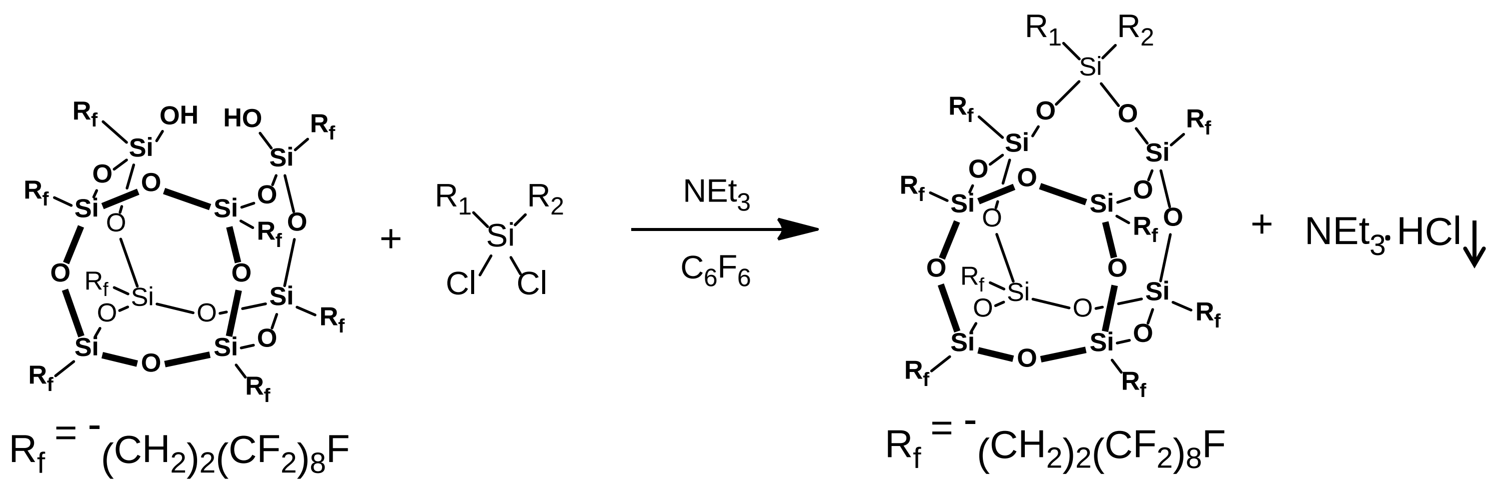
F-POSS cage array: 3 dimers (6 cages) – top view

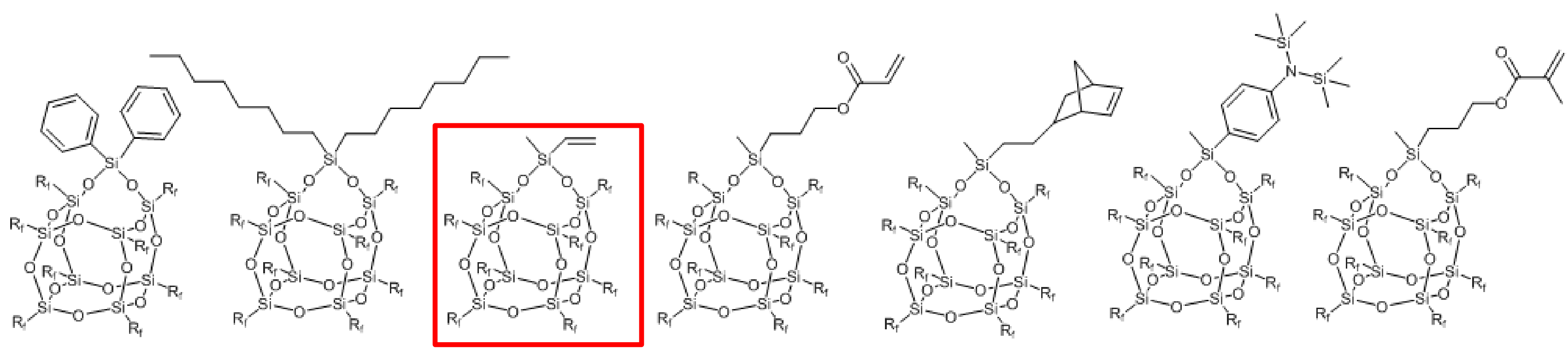


F-POSS cage "zigzag" array (16 cages) – top view



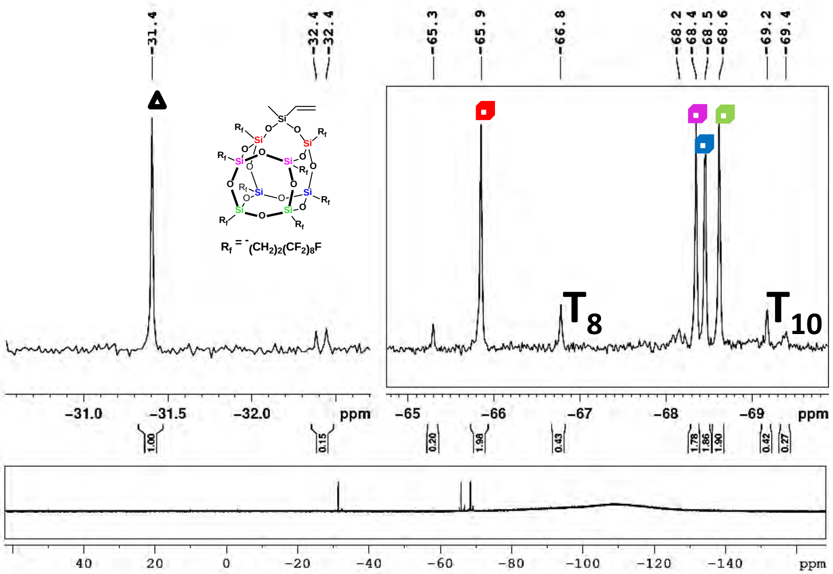
Functional Fluorodecyl POSS Synthesis from Incompletely Condensed Fluorodecyl POSS

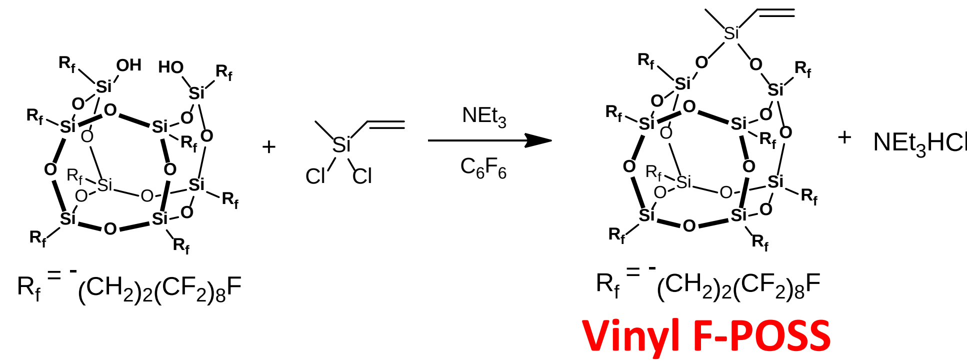


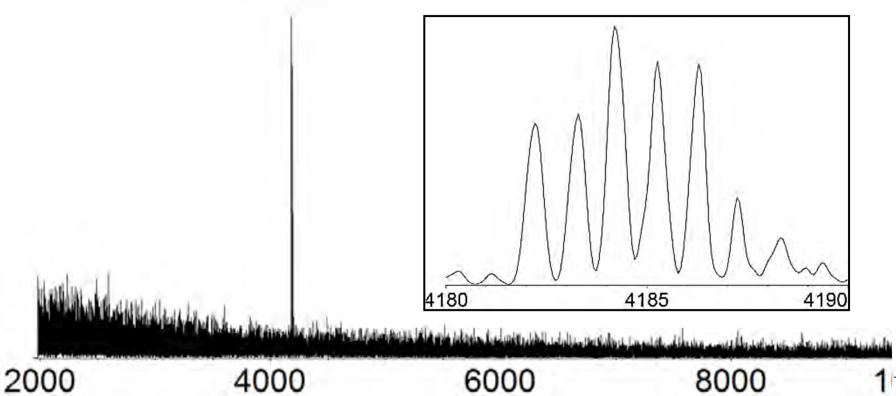


Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS,* **2011**, *133*, 20084.

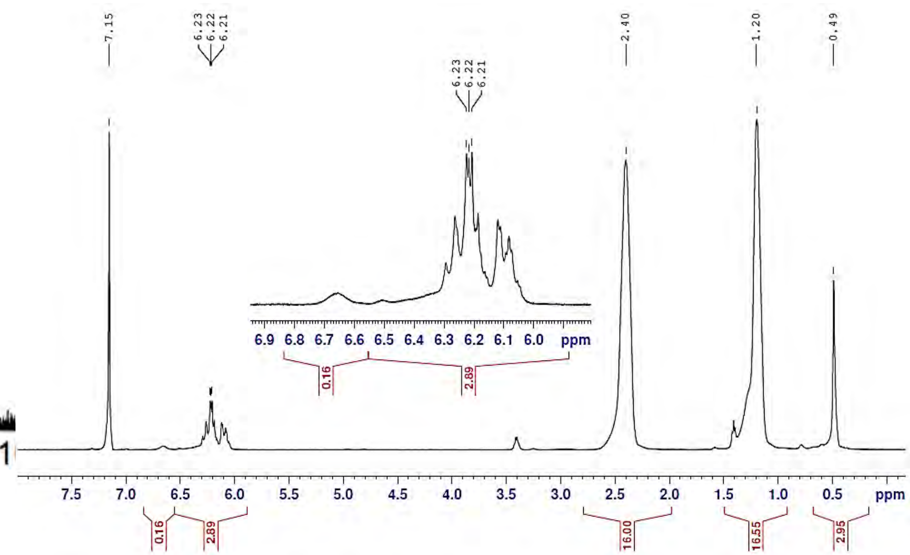
Fluorodecyl$_8$T$_8$D$_1$(methyl, vinyl) POSS



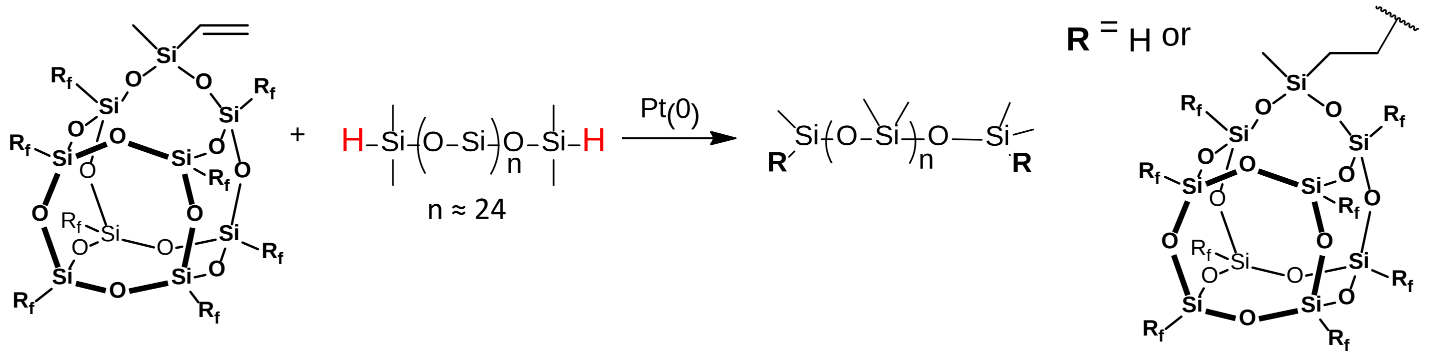




Theoretical $[M\cdot Ag]^+$ = 4185.71 Da



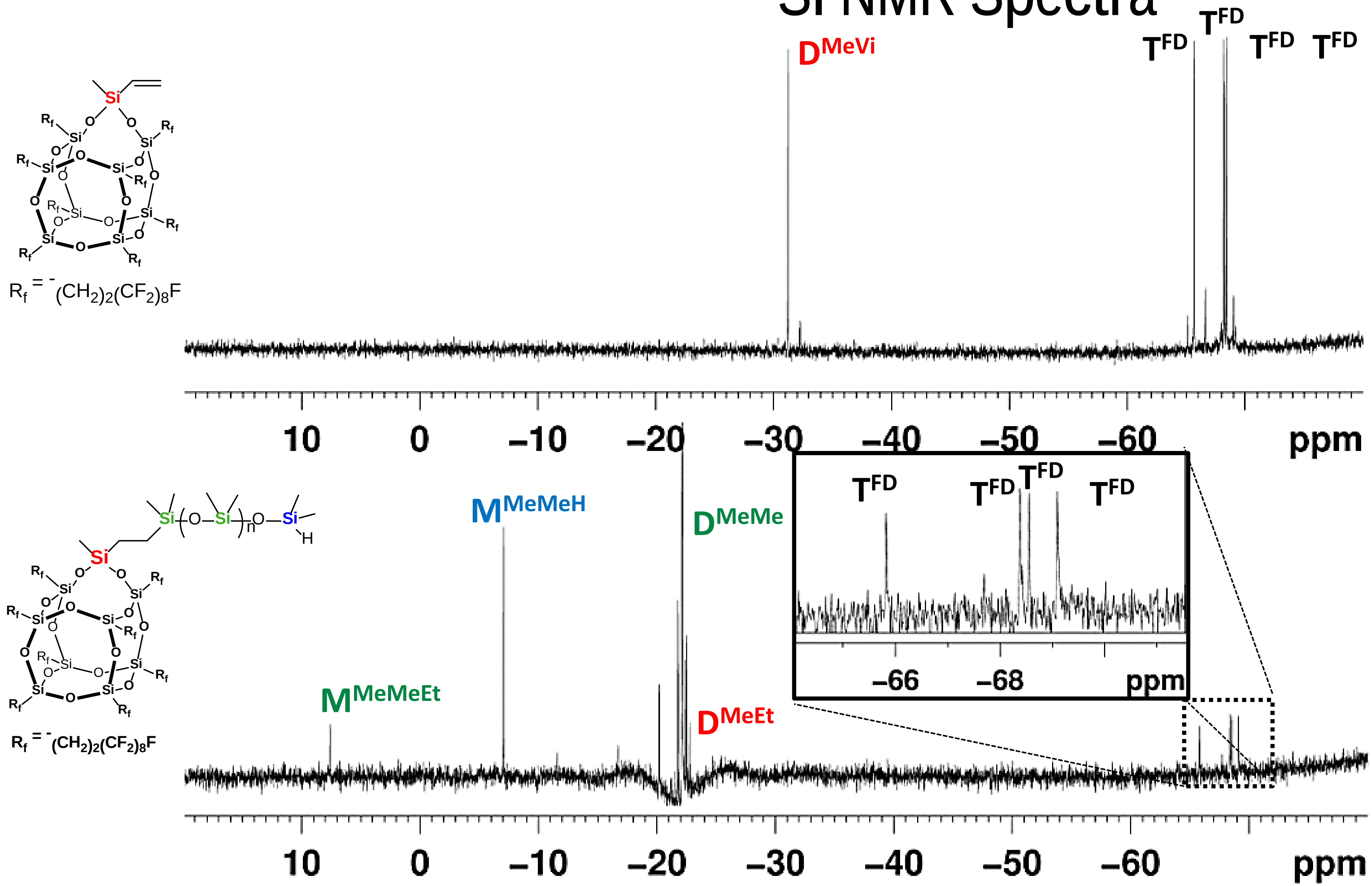
F-POSS Grafting to PDMS via Hydrosilylation



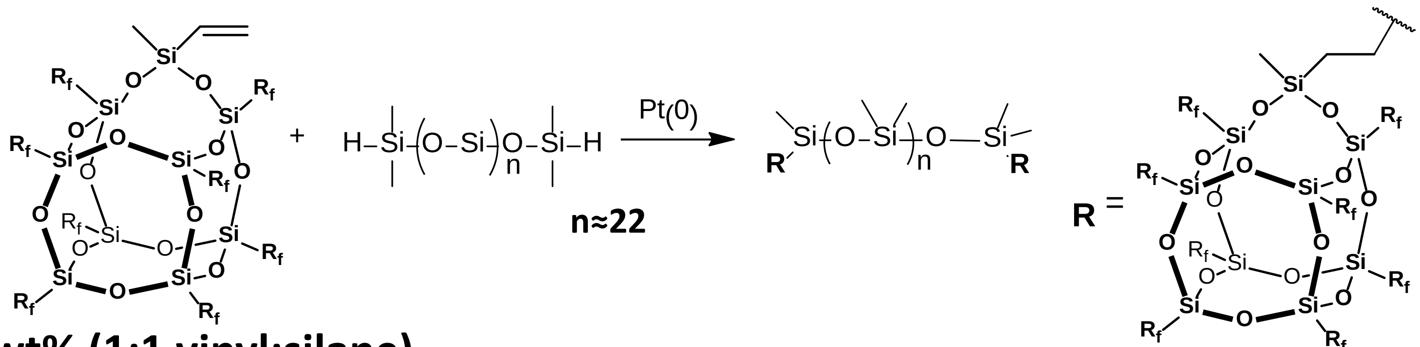
1, 5, 10, 20, 44 wt%

<u>Vinyl: silane</u>, 1:32, 1:8, 1:4, 1:2, 1:1

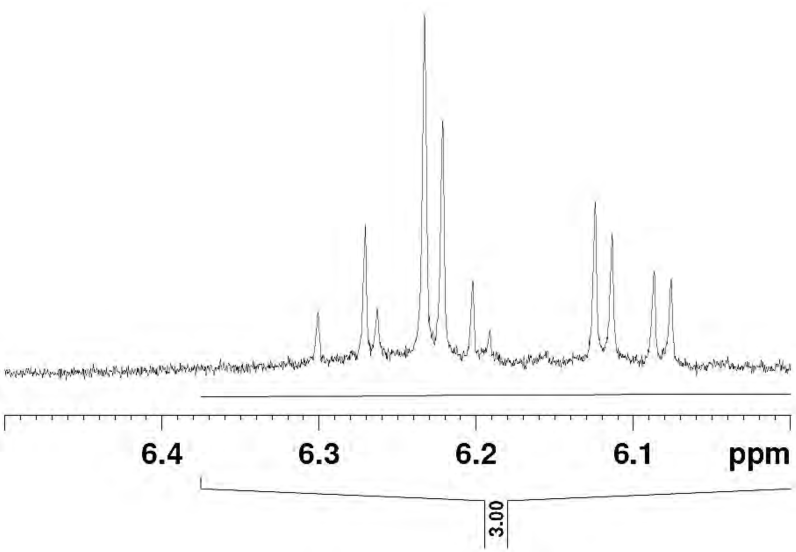
Complete Conversion at 10 wt% F-POSS: ^{29}Si NMR Spectra

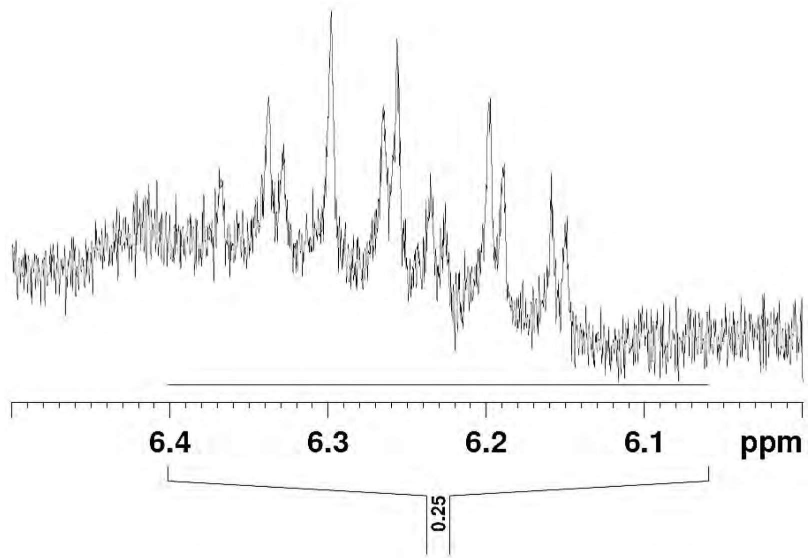


Incomplete Conversion at ≥20 wt% F-POSS: ^{1}H NMR Spectra

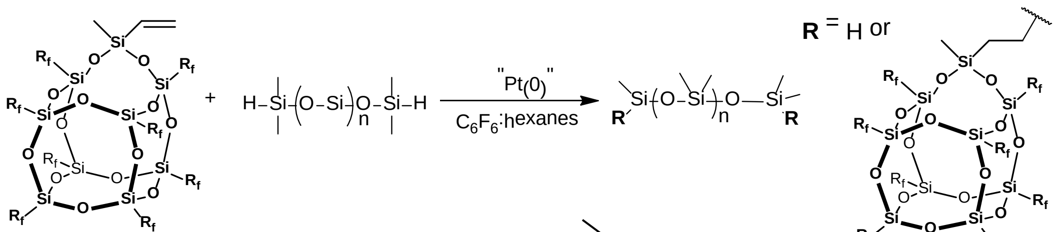


44 wt% (1:1 vinyl:silane)



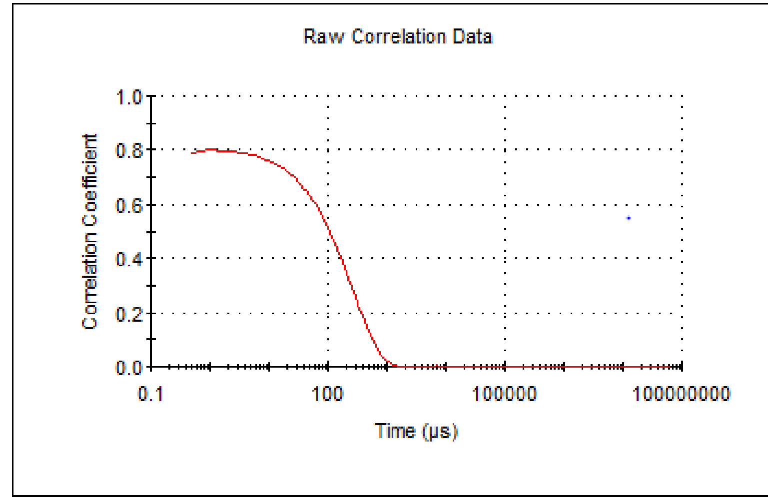


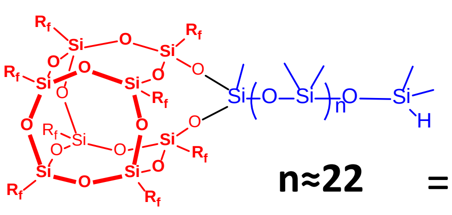
F-POSS PDMS Amphiphile Aggregation



44 wt% (2 mol eq.)

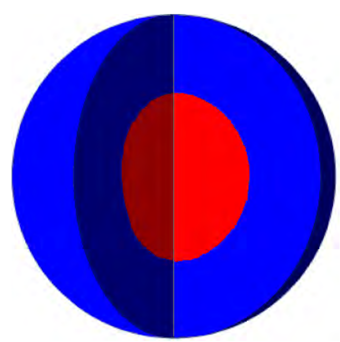
Crude rxn. mix.
4:1 C_6F_6:hexanes

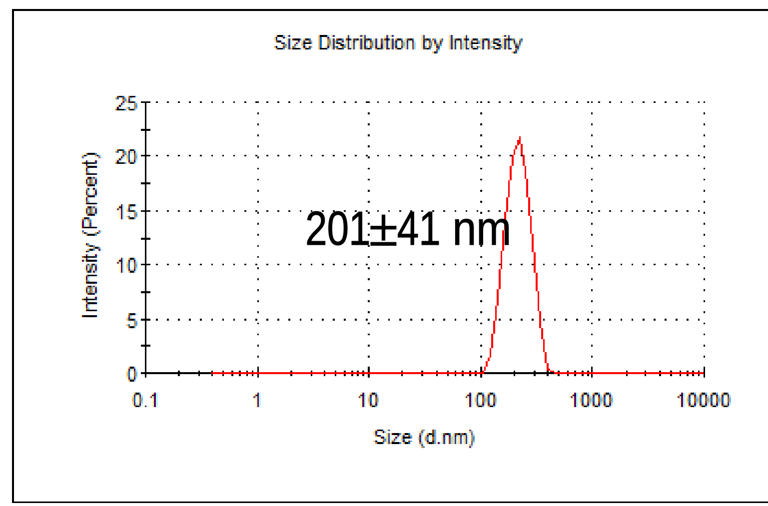




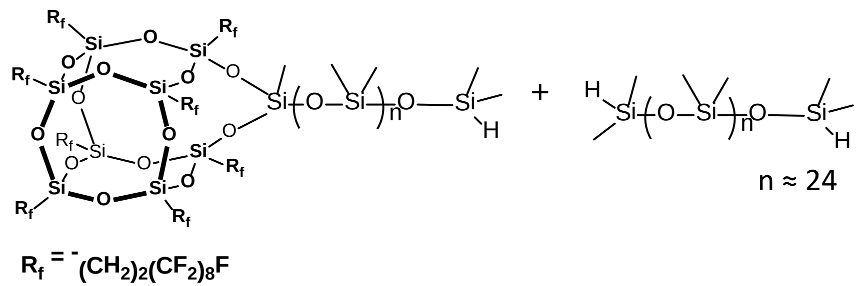
$R_f = {}^{-}(CH_2)_2(CF_2)_8F$

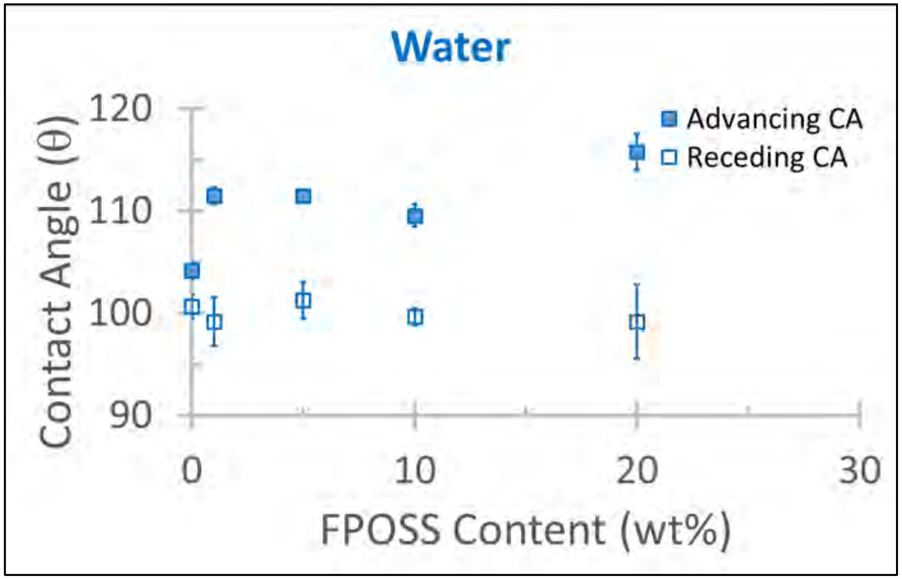
n≈22 =

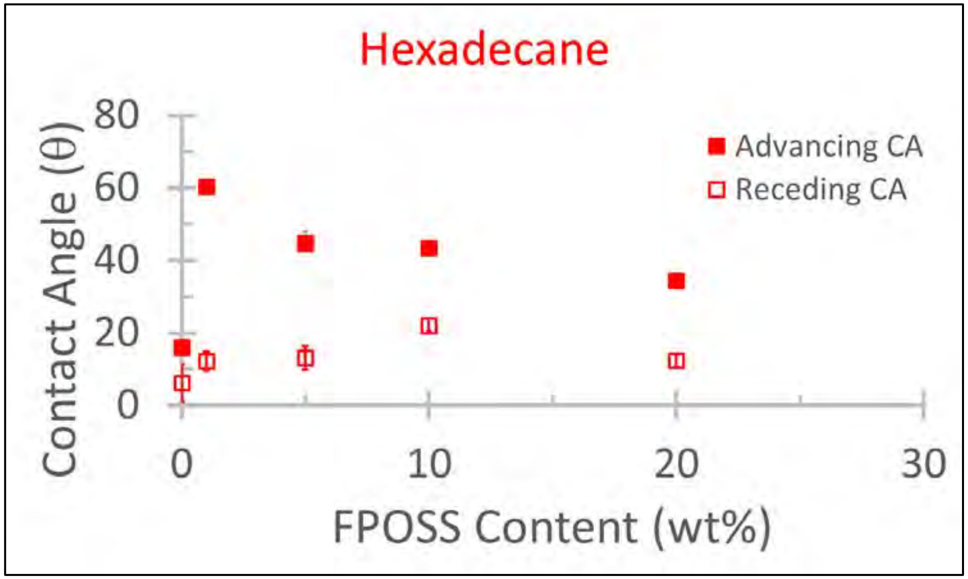




Surface Wetting of Fluorodecyl POSS -PDMS Amphiphiles



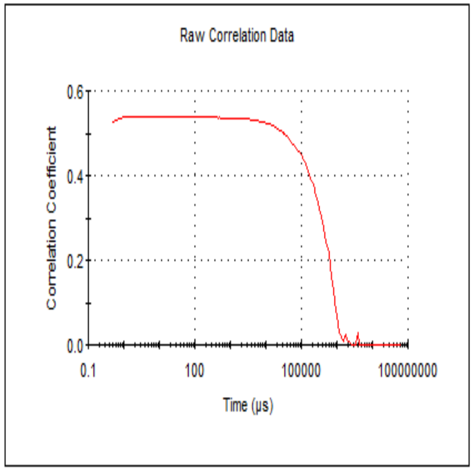


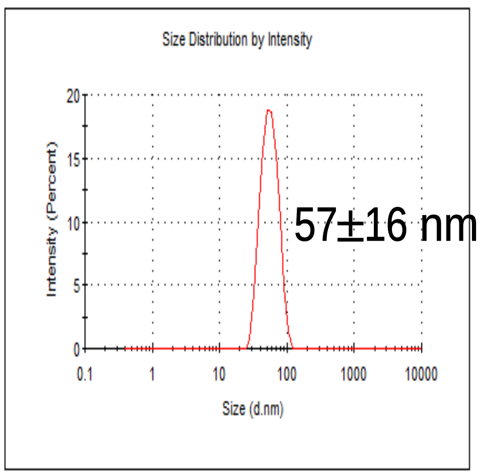


Pure fluorodecyl$_8$T$_8$ POSS: Water $\theta_{adv}/\ \theta_{rec}$ = 124°/116°

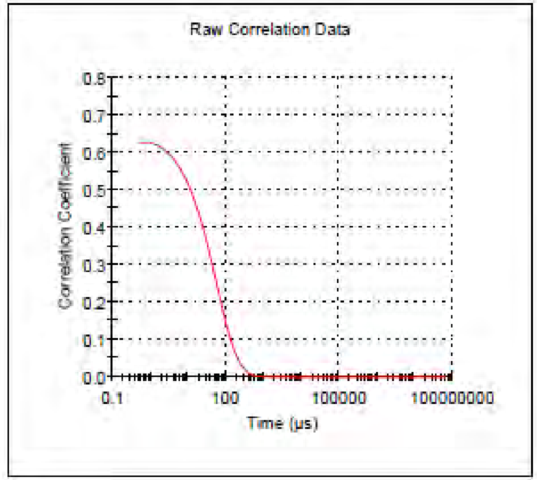
Hexadecane$\theta_{adv}/\ \theta_{rec}$ = 80°/61°

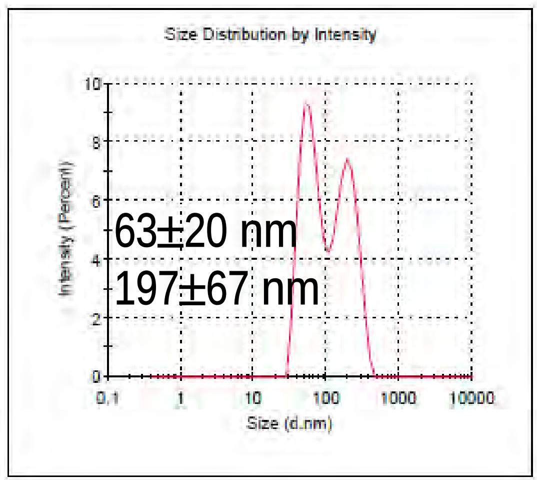
F-POSS PDMS Amphiphile Aggregation: Dynamic Light Scattering



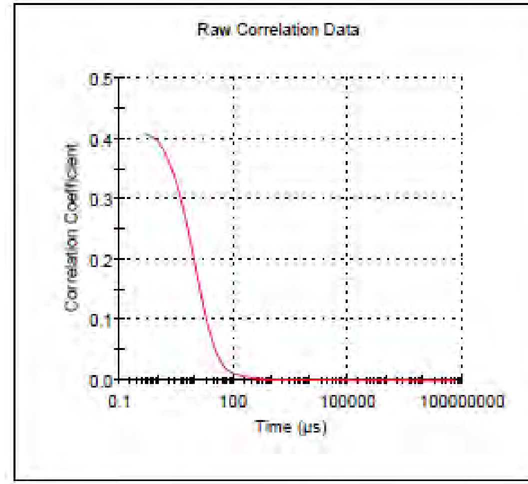


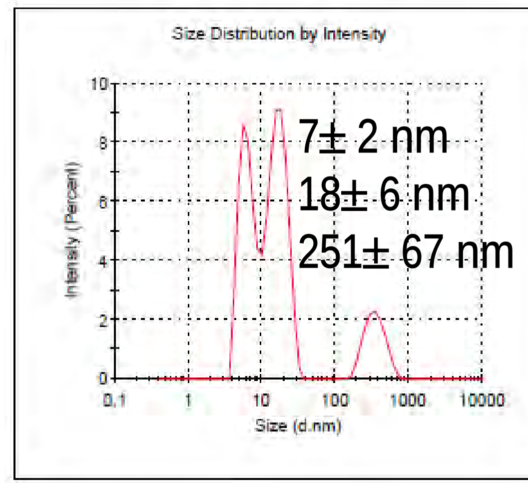
PDMS (1000 cSt)
0.001 M, 25 C





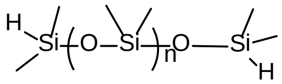
CDCl3
0.001 M, 25 C



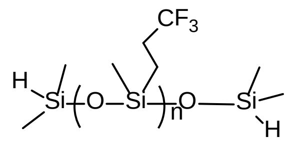


AK225
0.001 M, 25 C

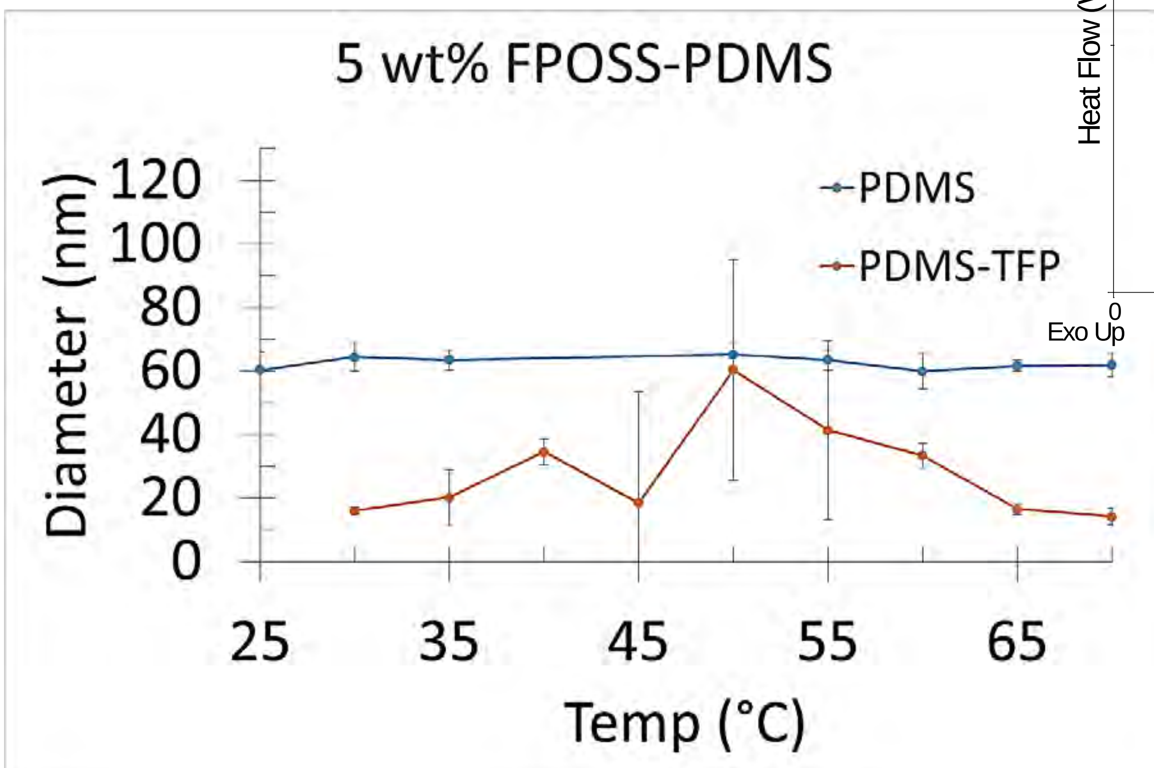
Thermal Stability of FPOSS-PDMS Micelles

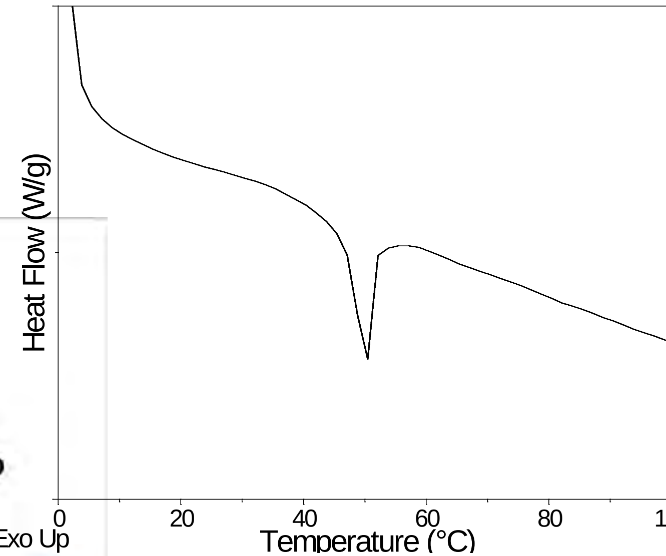


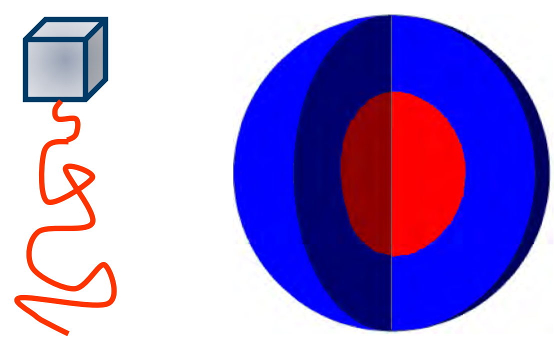
PDMS



PDMS-TFP

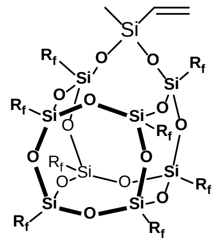






In fluorinated matrix

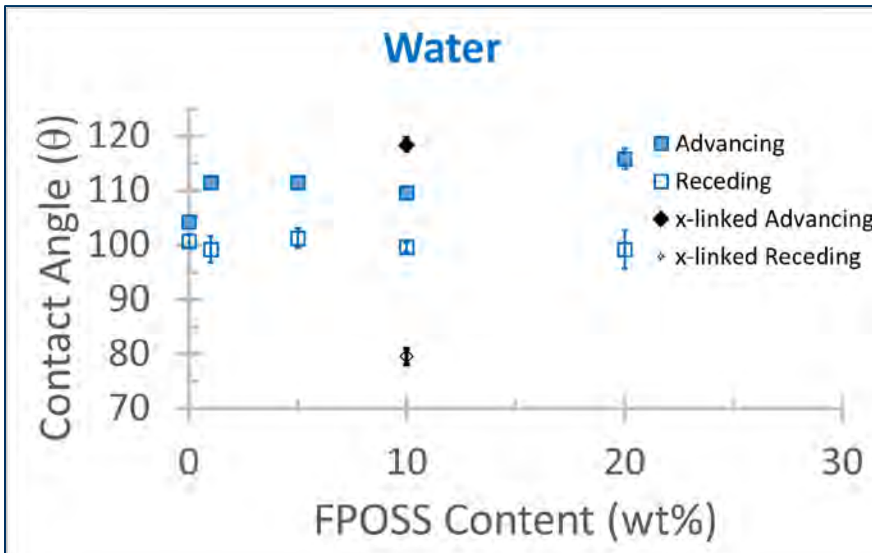
Surface Wetting of Fluorodecyl POSS-Enchained PDMS Elastomers

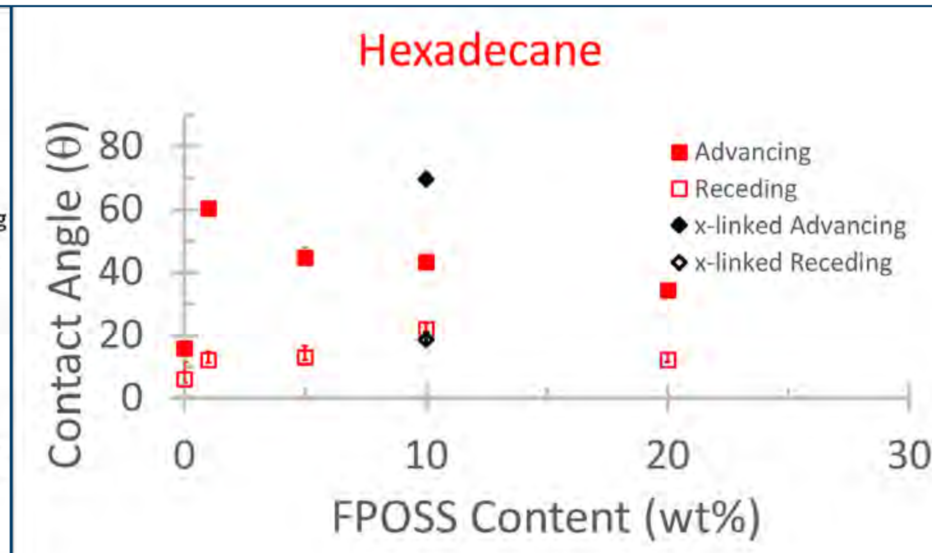


$R_f = -(CH_2)_2(CF_2)_8F$

\+ Sylgard 184
10:1 base:curative

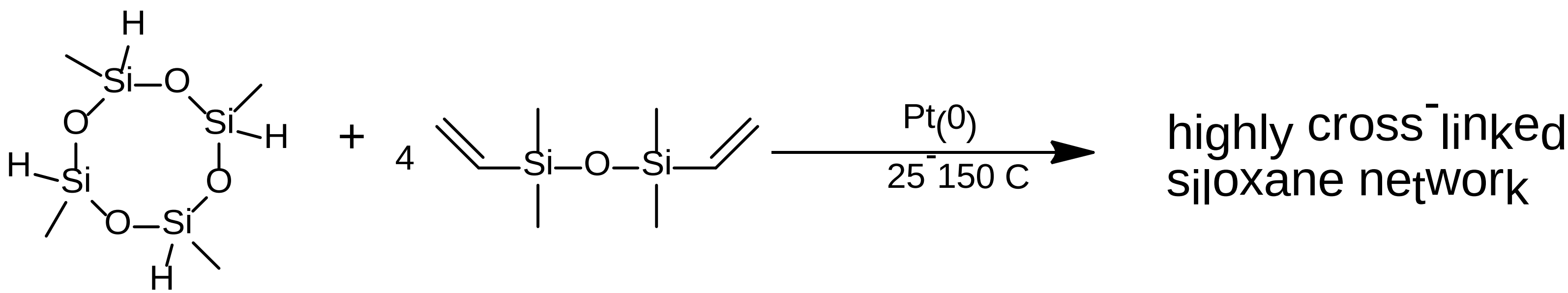
$\xrightarrow[\text{45 °C/17 hrs}]{\text{70 °C/4 hrs,}}$ F-POSS enchained PDMS Elastomer
(Black diamonds in figures)





Pure fluorodecyl$_8$T$_8$ POSS: Water $\theta_{adv}/\ \theta_{rec}$ = 124°/116°
Hexadecane $\theta_{adv}/\ \theta_{rec}$ = 80°/61°

Surface modification of highly crosslinked siloxane networks

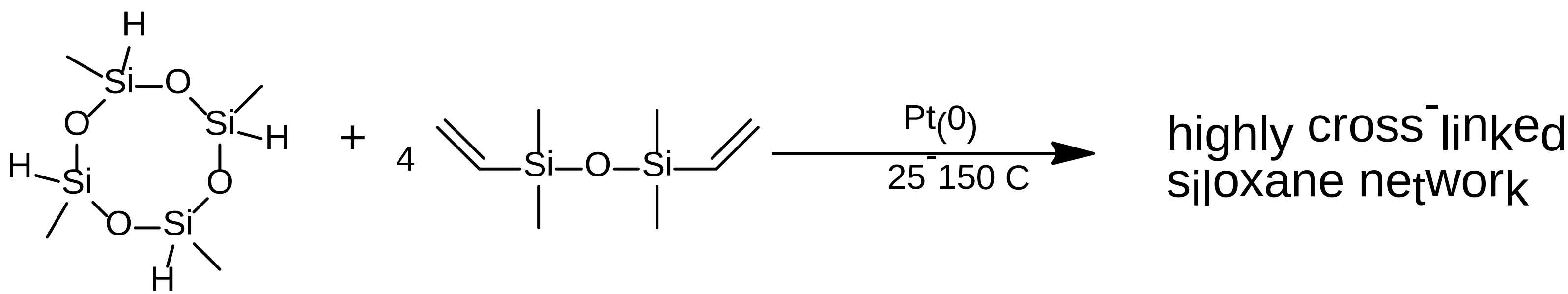


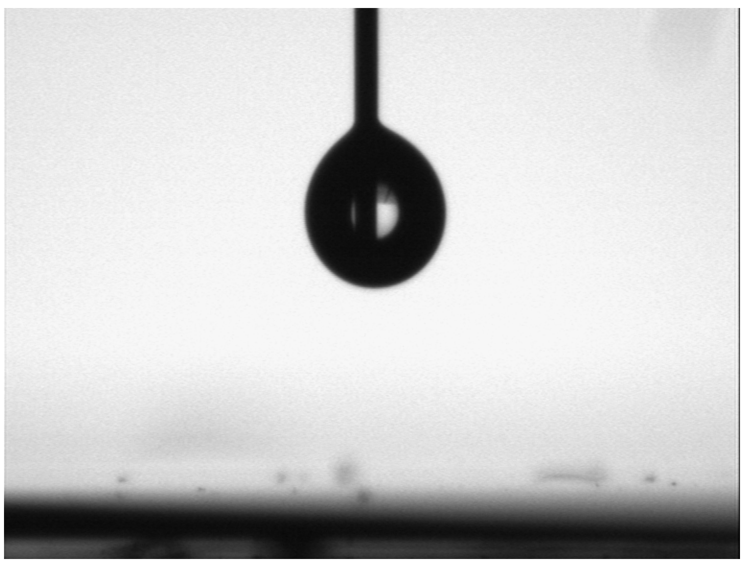
ethanol Θ_{stat}/ Θ_{adv}/ Θ_{rec} = 8.9
22.88 ± 2.46
0

isopropanol completely wets and spreads

	θ_{adv}/ θ_{rec} (°)
Water	99.5 ± 0.6 / 93.2 ± 0.5
Hexadecane	33.6 ± 0. 3 / 28.9 ± 0.3
Heptane	<5 / 0
methanol	29.3 ± 0.5 / 18.3 ± 2.4

Surface modification of highly crosslinked siloxane networks





	θ_{adv}/ θ_{rec} (°)
Water	99.5 ± 0.6 / 93.2 ± 0.5
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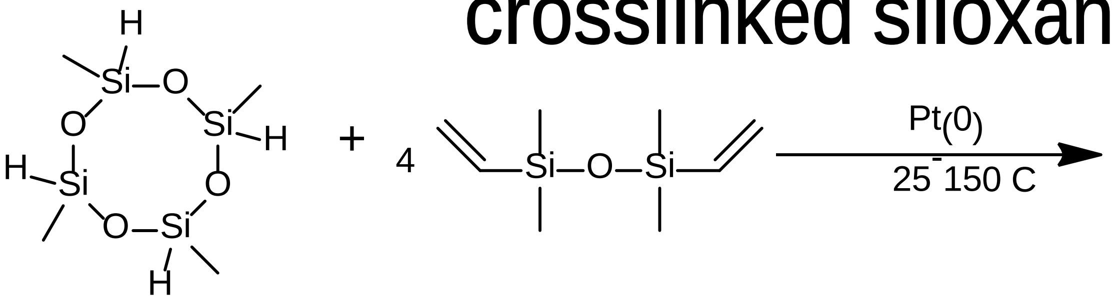
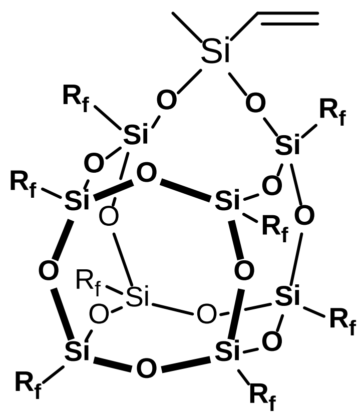
Surface modification of highly crosslinked siloxane networks



highly cross-linked siloxane network w/ covalently-bound FPOSS surface

+ 1 wt%



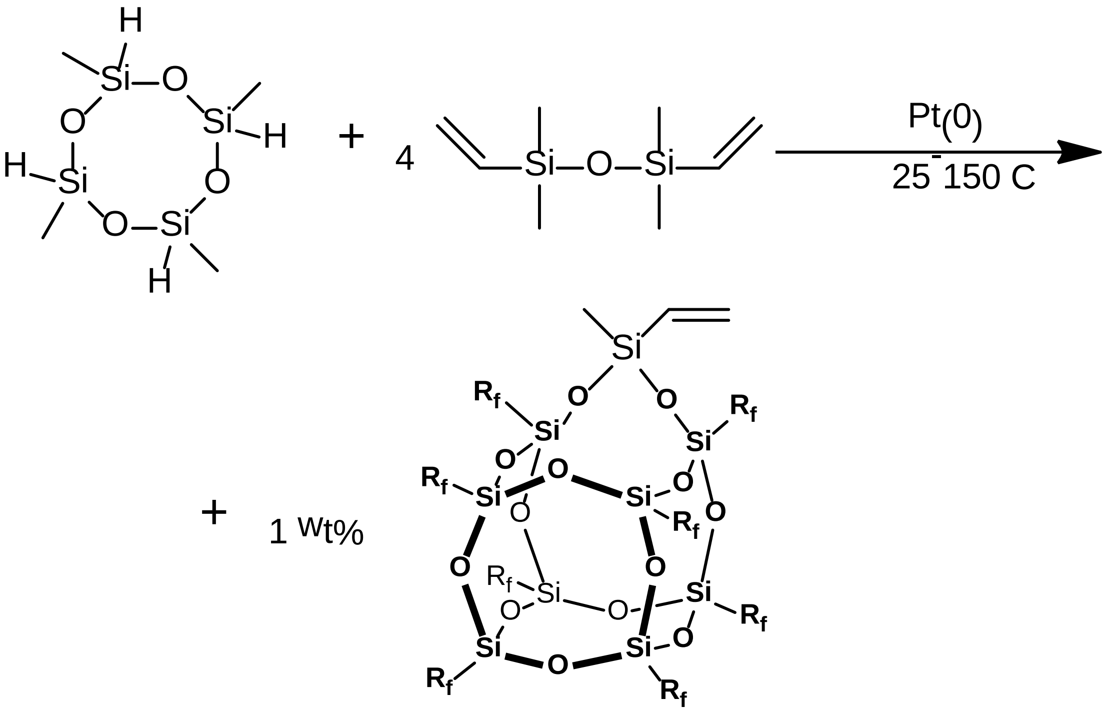
(**0.63 wt% fluorine**) $R_f = -(CH_2)_2(CF_2)_8F$

isopropanol Θ_{stat}/ Θ_{adv}/ Θ_{rec} = 54.35 ± 4.41
70.94 ± 1.05
40.5 ± 0.86

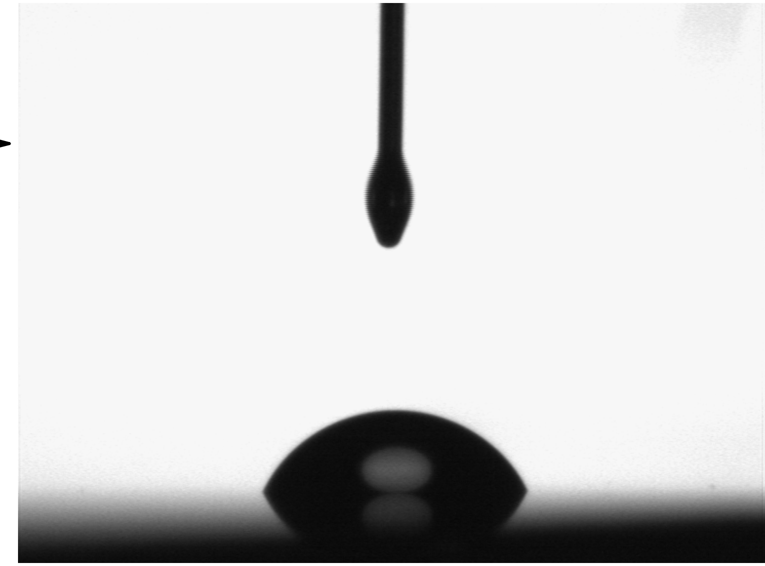
ethanol Θ_{stat}/ Θ_{adv}/ Θ_{rec} = 60.588 ± 7.62
73.97 ± 1.0075
41.4 ± 1.2725

	θ_{adv}/ θ_{rec} (°)
Water	116.5 ± 0.3 / 102 ± 1.1
Hexadecane	76.3 ± 0.5 / 62 ± 1.0
Heptane	56.1 ± 0.9 / 39.2 ± 1.2
methanol	75.2 ± 0.9 / 49.9 ± 1.5

Surface modification of highly crosslinked siloxane networks



$R_f = -(CH_2)_2(CF_2)_8F$

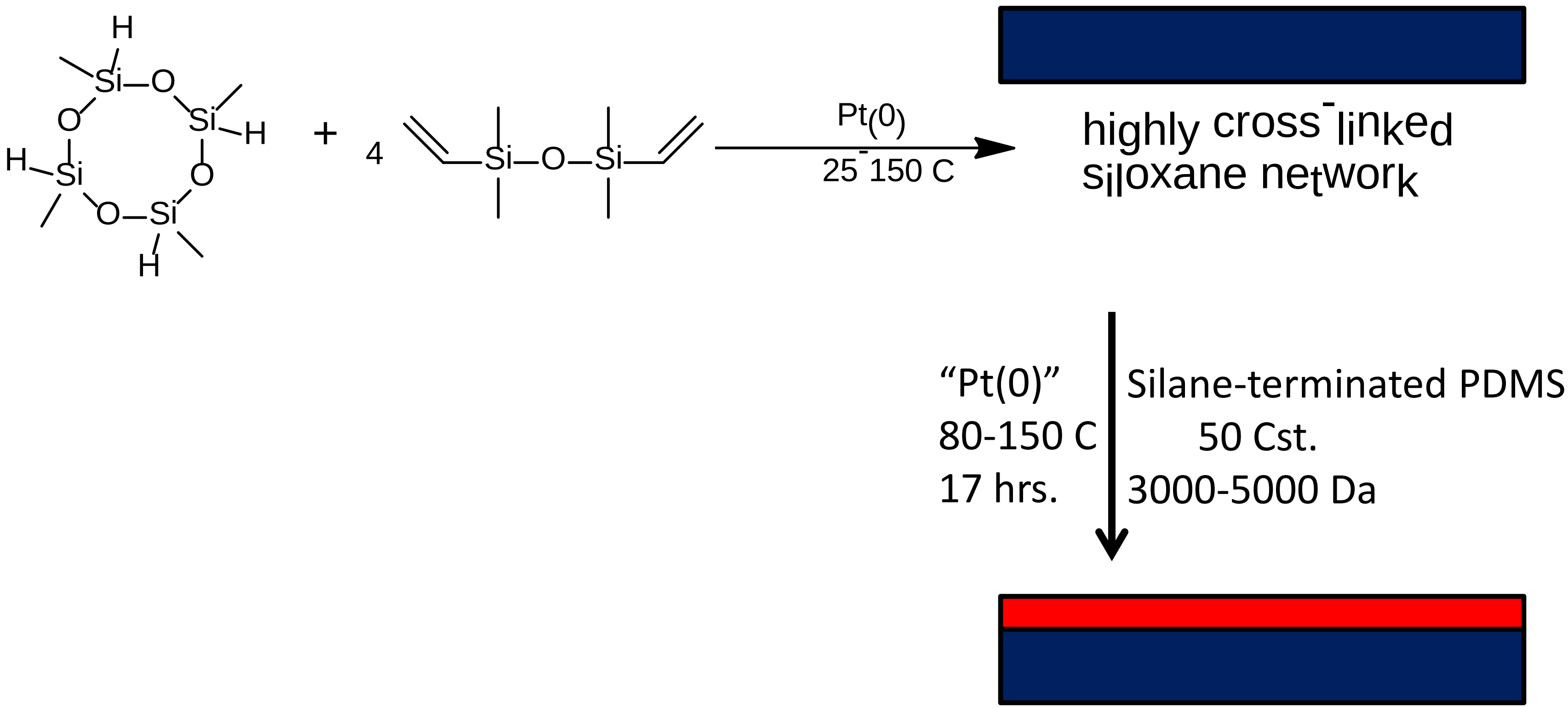


	θ_{adv}/ θ_{rec} (°)
Water	116.5 ± 0.3 / 102 ± 1.1
Hexadecane	76.3 ± 0.5 / 62 ± 1.0
Heptane	56.1 ± 0.9 / 39.2 ± 1.2
methanol	75.2 ± 0.9 / 49.9 ± 1.5

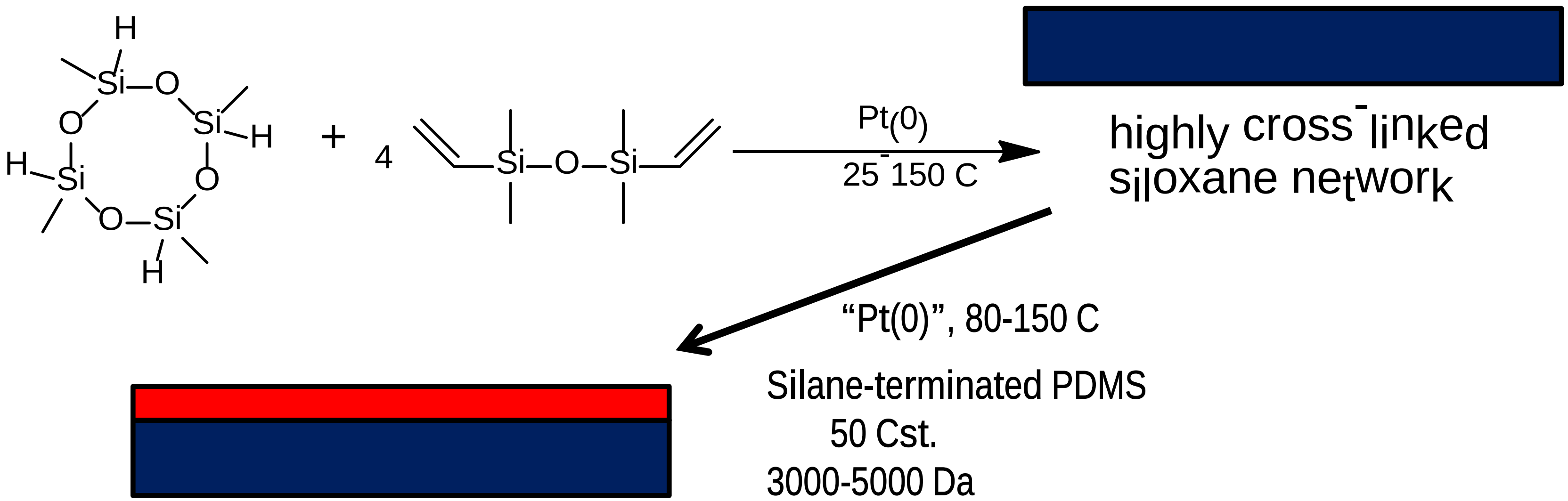
What about “liquid-like” surfaces and post-cure surface modification?

…….

Post-cure surface modification of highly crosslinked siloxane networks with silane-term oligo(dimethylsiloxane)



Post-cure surface modification of highly crosslinked siloxane networks with silane-term oligo(dimethylsiloxane)



	θ_{adv}/ θ_{rec} (°)
Water	110.7 $\pm$ 0.3 / 89.4 $\pm$ 0.5
Hexadecane	47.8 $\pm$ 0.4 / 17.5 $\pm$ 0.7
Heptane	7.3 $\pm$ 1.9 / 0
methanol	40.8 $\pm$ 0.4 / 35.5 $\pm$ 0.6

	θ_{adv}/ θ_{rec} (°)
Water	99.5 $\pm$ 0.6 / 93.2 $\pm$ 0.5
Hexadecane	33.6 $\pm$ 0. 3 / 28.9 $\pm$ 0.3
Heptane	<5 / 0
methanol	29.3 $\pm$ 0.5 / 18.3 $\pm$ 2.4